Figure 3-36-2—A pair of 10-in. C-½Mo flanged pipe sections (SA335-P1 and SA234-WP1) from a hot bypass line in a catalytic reformer that was designed to remain closed but operated partially or fully open for unknown lengths of time. They were in service for ~34 years at temperatures up to 960 °F (515 °C) with a hydrogen partial pressure of 198 psig (1.4 MPa).

Figure 3-36-3—A photomicrograph of the OD surface of a pipe section from Figure 3-35-2 exhibits a normal ferritic-pearlitic microstructure. Magnification 200X.

Figure 3-36-4—A photomicrograph at the ID surface of the pipe in Figure 3-35-2 shows complete decarburization of the original structure. Magnification 200X.

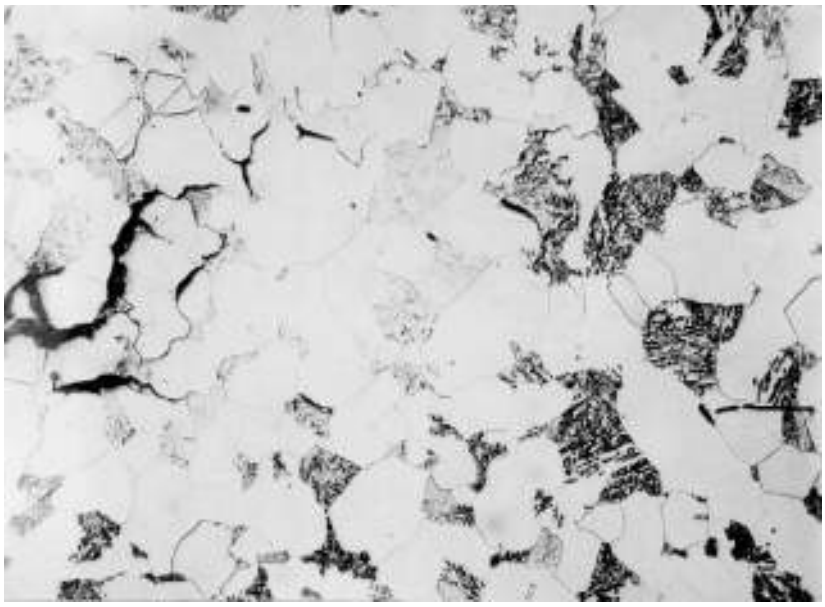


Figure 3-36-5—A photomicrograph illustrating internal decarburization and fissuring of C-½Mo steel.

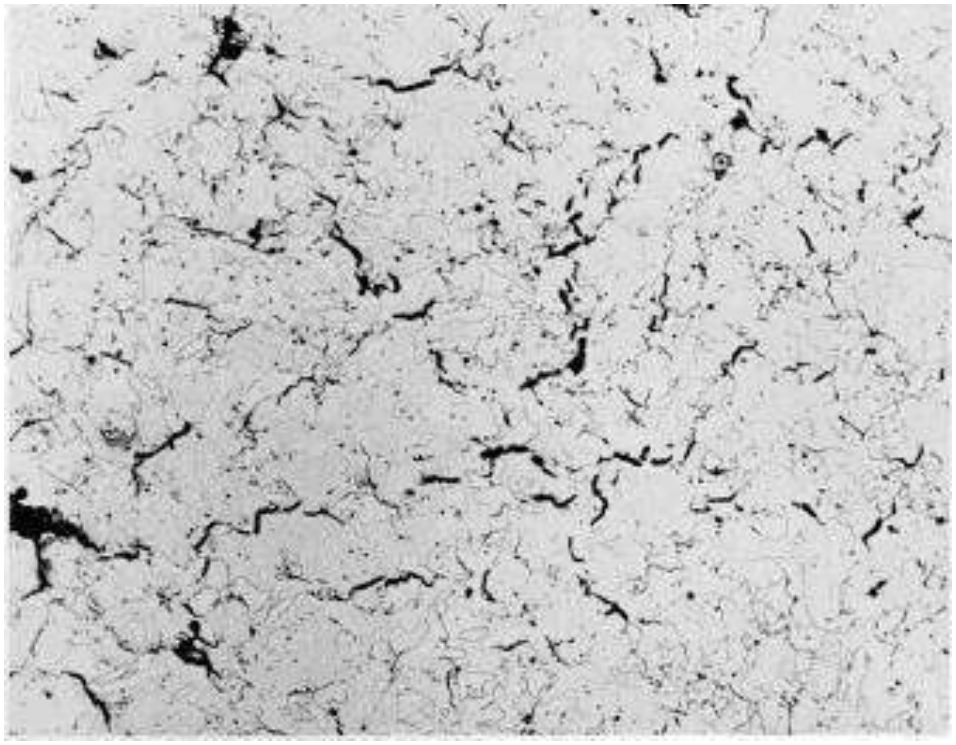


Figure 3-36-6—A high-magnification photomicrograph showing linkup of microfissures to form continuous cracks. Note that damage is accompanied by a significant amount of internal decarburization.

3.37 Hydrochloric Acid Corrosion

3.37.1 Description of Damage

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

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

3.37.2 Affected Materials

All common materials of construction used in refineries.

3.37.3 Critical Factors

a) HCl acid concentration, temperature, and alloy composition.

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

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

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

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

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

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

3.37.4 Affected Units or Equipment

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

a) Crude units.

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

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

b) Hydroprocessing units.

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

2. Ammonium chloride salts can form in various parts of the unit, including the effluent side of the hot feed/effluent exchangers because both NH_3 and HCl are present and they may condense with water in the effluent train.

3. HCl-containing streams can migrate through the fractionation section, resulting in severe acid dew point corrosion at the mixing point where the stream contacts water.

c) Catalytic reforming units.

1. Chlorides may be stripped from the catalyst and react to form HCl that carries through the effluent train, regeneration system, stabilizer tower, debutanizer tower, and feed/preheat exchangers.

2. HCl-containing vapors can migrate through the gas plant fractionation section, resulting in corrosion at mix points where HCl-containing vapor streams mix with streams containing free water. HCl corrosion can also occur in these streams where they cool below the acid dew point and in water boots and lines off the water boots.

3.37.5 Appearance or Morphology of Damage

a) Carbon steel and low-alloy steels suffer uniform thinning, localized corrosion, or under-deposit attack.

b) 300 series SS and 400 series SS will often suffer pitting attack, and 300 series SS may experience Cl^- SCC if the temperature is sufficiently high. (See 3.17.)

3.37.6 Prevention/Mitigation

a) Crude units.

1. Optimizing the crude oil tank water separation and withdrawal and crude desalting operation will help reduce chloride content in the feed to the crude tower. A common target is 20 ppm or fewer chlorides in the overhead accumulator water.

2. Upgrading carbon steel to nickel-based alloys or titanium can reduce HCl acid corrosion problems.

3. Water wash can be added to quench the overhead stream and to help dilute the condensing hydrochloric acid concentration.

4. Caustic injection downstream of the desalter is another common method used to reduce the amount of HCl going overhead. Proper design and operating guidelines should be followed to avoid caustic SCC (3.15) and fouling in the feed preheat train.

5. Various combinations of ammonia, neutralizing amines, and filming amines can be injected in the atmospheric tower overhead line before the water dew point.

6. Well-maintained process monitoring locations, e.g. for measuring chloride content, water injection rates, and chemical injection rates, are important for managing HCl corrosion.

b) Hydroprocessing.

1. Carryover of water and chloride salts, including neutralizing amine hydrochloride salts, should be minimized

2. HCl in H_2 streams should be minimized (e.g. by installing scrubbers or guard beds to remove HCl from hydrogen produced in catalytic reforming units).

3. Corrosion-resistant nickel-based alloys should be used where necessary.

4. Well-maintained process monitoring locations are important for minimizing the effects of HCl corrosion.

c) Catalytic reforming.

1. Same as hydroprocessing, but in addition, water washing the hydrocarbon stream has also been used to remove the highly water-soluble chlorides. Special care in the design and operation of this equipment is needed. Minimizing water and/or oxygenates in the feed will reduce stripping of chlorides from the catalyst.

2. Special adsorbents in chloride beds and chloride treaters can be used to remove chlorides from the recycle hydrogen streams and from liquid hydrocarbon streams.

3. Well-maintained process monitoring locations are important for minimizing the effects of HCl corrosion.

3.37.7 Inspection and Monitoring

a) Hydrochloric acid causes both general and localized corrosion and is very aggressive to most common materials of construction, especially carbon steel, across a wide range of concentrations.

b) Where applicable, VT should be performed on all accessible components with the potential for hydrochloric acid corrosion. These areas of concern can be characterized by orange-yellow discoloration of the affected material with scale buildup and various levels of deterioration.

c) UT thickness mapping, including AUT, can be utilized to determine the extent of localized thinning.

d) RT can be utilized to find or monitor localized thinning in piping components. RT is often performed at transition components (e.g. elbows, three-way or four-way fittings, and dead-legs).

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

f) Permanently mounted thickness monitoring sensors can be used.

g) The pH of the water in the boot of the atmospheric tower overhead accumulator should be checked regularly. Other variables including chloride and iron content are typically checked on a less frequent basis but do need to be monitored regularly. The water draws from fractionator and stripper tower overhead drums in hydroprocessing and catalytic reformer units should also be checked regularly.

3.37.8 Related Mechanisms

Ammonium chloride corrosion (3.6), Cl^- SCC (3.17), and aqueous organic acid corrosion (3.7).

3.37.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.

2. A. Bagdasarian et al., “Crude Unit Corrosion and Corrosion Control,” Paper No. 615, *Corrosion/96*, NACE International, Houston, TX.

3. NACE Publication 34105, *Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling*, NACE International, Houston, TX.

3.38 Hydrofluoric Acid Corrosion

3.38.1 Description of Damage

Corrosion by water containing dilute hydrofluoric (HF) acid can result in high rates of general or localized corrosion and may be accompanied by hydrogen cracking, blistering, and/or HIC/SOHIC. (See 3.41 and 3.67.) In refining, it is associated with HF acid alkylation units.

3.38.2 Affected Materials

a) Carbon steel, copper-nickel alloys, Alloy 400.

b) Low-alloy steels, 300 series SS, and 400 series SS are susceptible to corrosion and/or cracking and are generally not suitable for HF service.

c) Nickel-based alloys such as Alloy C276 have been used in some applications.

3.38.3 Critical Factors

a) HF acid concentration (water content), temperature, alloy composition, and the presence of contaminants including oxygen and sulfur compounds are the controlling factors.

b) Corrosion rates increase with increasing temperature and decreasing HF concentration (increasing water content), as shown in Figure 3-38-1 and Figure 3-38-2.

c) Carbon steel forms a protective fluoride scale in dry (anhydrous), fresh HF, which enables a very low general corrosion rate in anhydrous HF.

d) HF containing dissolved water (rich HF) is created when the fresh acid has picked up water as it encounters residual moisture in the feed and isobutane entering an HF alkylation unit. This water-bearing acid can still form a tight protective fluoride scale on carbon steel (e.g. in the reactor settler circuit) but can be impacted by:

   1. water content, which if operated at > 1.5 wt % in acid can increase the general corrosion rates; and

   2. higher temperatures, which can increase the general corrosion rates.

e) Rich HF (e.g. as sent to regeneration or as carryover into fractionation), when subject to a phase change (vaporization and condensation), can cause significant localized corrosion of carbon steel because the phase-changing rich HF reaches a very corrosive azeotropic concentration. (An azeotrope is a constant boiling temperature mixture of liquids.) The amount and location of corrosion are impacted by:

   1. the amount of water in the rich HF, which will determine the amount of corrosive azeotrope that can form;

   2. the amount of rich HF carryover, as determined by reactor circuit operating conditions, with greater amounts of rich HF contributing to increased amounts of azeotrope formation; and

   3. changes in the temperature and pressure profiles in the fractionation section, which will determine locations where phase changes occur.

f) Streams with entrained rich HF, such as in the fractionation overhead system where phase changes do not occur, will be subject to general corrosion except for possible residual element (RE) effects.

g) Dead-legs in fractionation can be subject to localized corrosion and iron fluoride fouling under the following circumstances.

   1. In the upper sections of fractionation where entrained rich HF can reach phase change conditions in dead-legs. Operational parameters that contribute to rich HF carryover will increase the potential for dead-leg corrosion.

2. In the hotter, lower sections of fractionation where organic fluorides will thermally decompose into free HF, which can accumulate in extended dead zones (e.g. PSV headers) and combine with residual waters to cause localized corrosion and iron fluoride scaling. Operational parameters within the reactor/settler will determine the amount of fluorides available for contributing to this corrosion and fouling.

h) Regeneration of rich HF to remove water and acid soluble oils is done at elevated temperatures that require the use of Alloy 400, which can be subject to various corrosion exposures.

1. Preheating rich HF (feed or entrained in isobutane stripping medium) above 160 °F (70 °C) will trigger azeotropic corrosion and require the use of Alloy 400, which will be subject to a low level of general corrosion.

2. Within the regeneration/rerun column, the acid is concentrated into the azeotrope, which corrodes Alloy 400 at a higher rate. Higher temperatures will increase the corrosivity of this material.

3. Hot HF vapor from the regenerator/rerun column prior to cooling can cause corrosion of carbon steel or Alloy 400 if partial condensation occurs and there is still significant water in the vapor.

i) Downstream of alumina treaters/defluorinators, the stream is water rich with a small amount of HF that if allowed to condense prior to KOH treating will create dilute HF, which will cause localized corrosion condition on carbon steel. This corrosion can be impacted by:

1. breakthrough of free HF from the defluorinators, and

2. the cooling temperature profile through to the KOH treater.

j) The acid relief header (ARH) and acid relief neutralizer (ARN) will be exposed to potential dilution of rich HF, which will then cause higher carbon steel corrosion rates. This corrosion is impacted by:

1. moisture ingress into the ARH from nonacid streams or wet purge gases,

2. inadequate liquid knockout facilities or procedures to remove excess acid into the ARN, and/or

3. inadequate ARN neutralization facilities or procedures. Initial contact zones within the neutralizer often require Alloy 400 construction.

k) In carbon steel, the RE content of the base metal and weld metal may have an effect on corrosion rates in certain parts of the unit. This RE content refers to trace elements, primarily %C, %Cu, %Ni, and %Cr, that are present in carbon steel as the result of the steel manufacturing process. (References 1 to 4, 10) The impact of RE varies throughout the unit.

1. Higher-RE welds and components preferentially corrode in streams with a significant quantity of entrained rich HF.

2. Higher-RE welds in rich HF have been reported to corrode at higher rates, particularly at higher operating water levels or higher operating temperatures.

3. High-RE components and welds corrode at substantially higher rates in phase change (azeotropic) exposure zones.

4. Low-RE components and welds corrode at substantially higher rates when galvanically coupled to high-RE components in dilute HF exposure zones.

l) Industry guidelines regarding RE content have been developed and implemented into some industry consensus standards as indicated below. A more detailed discussion of these guidelines is outlined in References 1 and 2.

1. When %C ≥ 0.18 wt % (some base metals), (%Cu + %Ni) should be < 0.15 wt %.

2. When %C < 0.18 wt % (weld metal, some base metals), (%Cu + %Ni + %Cr) should be < 0.15 wt %.

m) Severe corrosion can occur when HF leaks into cooling water or steam due to the dilution of HF.

n) Oxygen contamination increases the corrosion rate of carbon steel and promotes accelerated corrosion and SCC of Alloy 400. (See 3.41.)

o) Modified HF (with additive) used in some units has unique corrosion factors that are not included in this discussion.

3.38.4 Affected Units or Equipment

a) Piping and equipment in the HF alkylation unit; flare piping and downstream units exposed to acid carryover are also affected.

b) Trace HF circuits can experience very high corrosion rates. A minimal amount of residual moisture can quickly yield a 10 % to 50 % HF acid-in-water concentration in a trace circuit, resulting in aggressive corrosion.

c) Most equipment is made from carbon steel with the exception of following, which are usually made partially or completely from Alloy 400.

1. Heated acid and acid-containing streams to the rerun/regenerator tower.

2. HF acid rerun/regenerator tower and ASO/CBM drain systems.

3. ARN acid/neutralizer contact zones.

d) High corrosion rates have been observed in:

1. piping and equipment operating above 150 °F (65 °C);

2. dead-legs including inlets to relief valves, as well as small-bore vents and drains; and

3. rich HF phase change locations including:

   — preheated feed exchangers and piping to the inlet of the isostripper, depropanizer, and HF stripper towers;

   — isostripper, depropanizer, and HF stripper tower tops; and

   — piping and exchangers off the top of the isostripper, depropanizer, and HF stripper or propane stripper where overhead vapors condense;

4. dead-legs, piping and exchangers between the alumina treaters/defluorinator and the KOH treater due to dilute HF exposure;

5. the ARH;

6. flange faces, particularly in rich HF phase change locations;

7. DMWs between Alloy 400 and CS in any acid service;

8. heat exchanger bundles that condense rich-HF-containing streams such as the isostripper overhead and recycle isobutane as well as the depropanizer overhead coolers; and

9. heat exchanger bundles that heat rich-HF-containing streams such as the acid vaporizer, isostripper, and depropanizer preheat exchangers.

e) Severe fouling due to iron fluoride corrosion product has been observed in:

1. the tops of the isostripper, depropanizer, and HF stripper towers as well as the piping and heat exchangers off of them; and

2. dead-legs (e.g. PSV headers) in the bottoms of the isostripper, depropanizer, and HF stripper towers.

3.38.5 Appearance or Morphology of Damage

a) Corrosion is in the form of:

1. general corrosion in fresh HF and rich HF,

2. localized corrosion of welds in rich HF,

3. localized corrosion in phase change rich HF,

4. localized corrosion in entrained rich HF,

5. general and localized corrosion of Alloy 400 in hot rerun/regenerator service,

6. localized corrosion in dead-legs in entrained rich HF or fluoride defluorination services,

7. localized corrosion in dilute HF, and

8. localized corrosion in the ARH and ARN.

b) Preferential corrosion may not always conform to behavior predicted by the RE guidelines in API 751. (Figure 3-38-3 to Figure 3-38-6)

c) DMWs between Alloy 400 and carbon steel will lead to preferential galvanic corrosion of the carbon steel (and potentially DMW cracking) if exposed to acid.

d) Corrosion may be accompanied by cracking due to hydrogen stress cracking, blistering, and/or HIC/SOHIC damage. (Figure 3-38-8)

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

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

g) Alloy 400 is susceptible to SCC when in contact with moist HF vapors in the presence of oxygen. (See 3.41.)

3.38.6 Prevention/Mitigation

a) Carbon steel operating above 150 °F (65 °C) should be closely monitored for loss in thickness and may need to be upgraded to Alloy 400.

b) Corrosion can be mitigated by careful unit operational controls such as:

1. maintaining strict controls on the water content of the circulating rich acid,

2. controlling the rate and temperature of the reactor/settler system,

3. minimizing acid carryover from the settler into fractionation,

4. controlling feed quality and the reactor to control fluoride formation,
5. controlling the temperature in fractionation to avoid phase changes outside of the exchangers,
6. controlling the temperature in the rerun/regenerator,
7. controlling HF stripper operation to avoid free HF into bottoms and defluorinators,
8. controlling the defluorinator to avoid free HF breakthrough and dilute HF condensation, and
9. controlling ARH and ARN neutralization to ensure full neutralization of relief streams.

c) PWHT of carbon steel can reduce the problems associated with SOHIC as well as minimizing accelerated preferential corrosion in the HAZ of welds.

d) Alloy 400 (solid or clad) can be used to eliminate the problems associated with blistering and HIC/SOHIC.

3.38.7 Inspection and Monitoring

a) UT can be used to monitor for corrosion loss. Because the carbon steel corrosion rate in HF acid can be highly localized, with rates having been found to vary as much as 30 % in a single component, AUT, hand scanning, or use of multiple single point readings per component may be needed for effective assessment.

b) Profile RT can be used to monitor for thickness loss in drains, vents, low points, swages, and small-bore piping, as well as fittings, where low-RE and high-RE materials are coupled.

c) PAUT can be used to perform in situ crevice corrosion monitoring on flange faces. The iron fluoride scale conforms to the shape of the flange face, which makes VT difficult when the flanges are separated.

d) GWT testing, while typically not providing the accuracy needed as compared to standard UT, can be a useful screening tool to identify locations for follow-up with UT.

e) Permanently mounted thickness monitoring sensors can be used.

f) Special emphasis programs to monitor RE corrosion, small-bore piping, mix point, dead-leg, and flange face corrosion (as well as blistering and HIC/SOHIC) are outlined in API 751.

g) RE content of carbon steel components should be monitored in accordance with API 751 guidelines. Potential localized corrosion of piping components and/or welds should be inspected for in accordance with API 751.

3.38.8 Related Mechanisms

Hydrogen stress cracking in HF acid (3.41), hydrogen blistering and HIC/SOHIC (covered in *Wet H_2S Damage* 3.67), HF acid SCC of nickel alloys (3.39), and DMW cracking (3.26).

3.38.9 References

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

2. NACE Publication 5A171, *Materials for Storing and Handling Commercial Grades of Aqueous Hydrofluoric Acid and Anhydrous Hydrogen Fluoride*, NACE International, Houston, TX.

3. H.H. Hashim and W.L. Valerioti, “Corrosion Resistance of Carbon Steel in HF Alkylation Service,” *Materials Performance*, November 1993, p. 50.

4. A. Gysbers et al., “Specification for Carbon Steel Materials for Hydrofluoric Acid Units,” Paper No. 03651, *Corrosion/2003*, NACE International, Houston, TX.

5. J.D. Dobis, D.R. Clarida and J.P. Richert, “Survey Reveals Nature of Corrosion in HF Alkylation Units,” *Oil and Gas Journal*, Vol. 93, No. 10, March 6, 1995, pp. 63–68.

6. H.S. Jennings, “Materials for Hydrofluoric Acid Service in the New Millenium,” Paper No. 01345, *Corrosion/2001*, NACE International, Houston, TX.

7. J.D. Dobis, D.G. Williams and D.L. Bryan Jr., “The Effect of Operating Conditions on Corrosion in HF Alkylation Units,” *Corrosion/04*, Paper No. 645, NACE International, Houston, TX, 2004.

8. J.D. Dobis, "The Top Ten Corrosion Issues Affecting HF Alkylation Units," Paper No. 07570, *Corrosion/2007*, NACE International, Houston, TX.

9. H.P.E. Helle, *Guidelines for Corrosion Control in HF-alkylation Units*, Second Edition, New Plantation, Delft, Netherlands, April 1993.

10. C.J. Schulz, Corrosion Rates of Carbon Steel in HF Alkylation Service,” Paper No. 06588, *Corrosion/2006*, NACE International, Houston, TX.

11. A.C. Gysbers, J. Wodarcyk, F. Sapienza, and T. Copeland, “Localized Corrosion of Carbon Steel from Hydrofluoric Acid—An Update,” *Materials Performance*, Vol. 56, No. 2, NACE International, Houston, TX, February 2017.

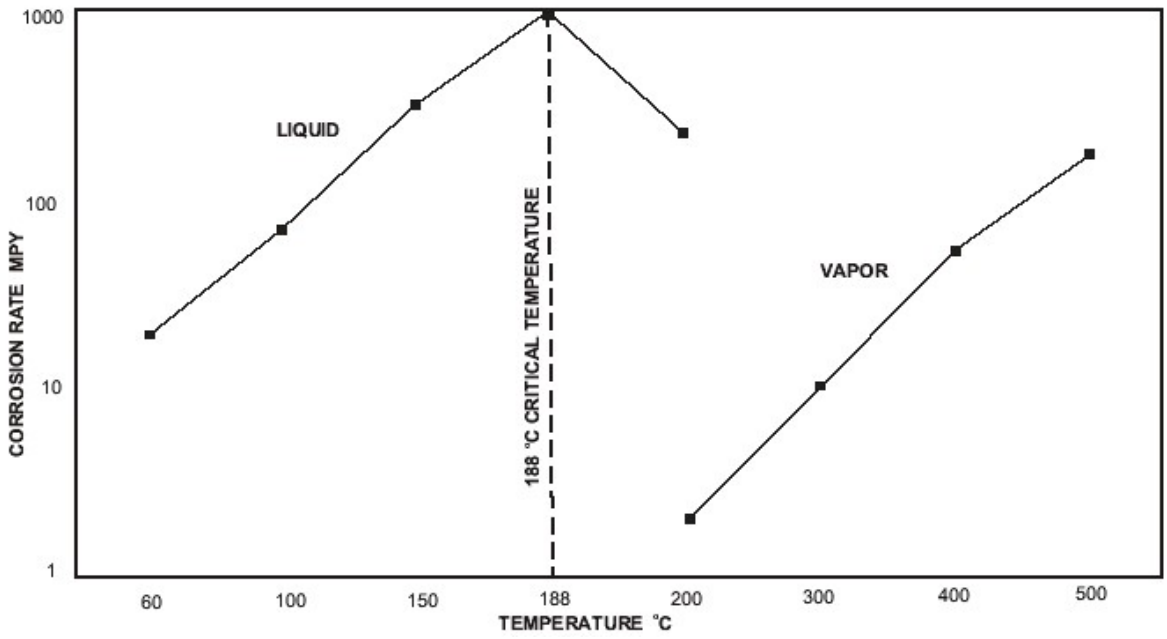


Figure 3-38-1—Corrosion rate as a function of temperature for carbon steel in anhydrous HF acid under stagnant conditions in 100-hr laboratory test. (Reference 2)

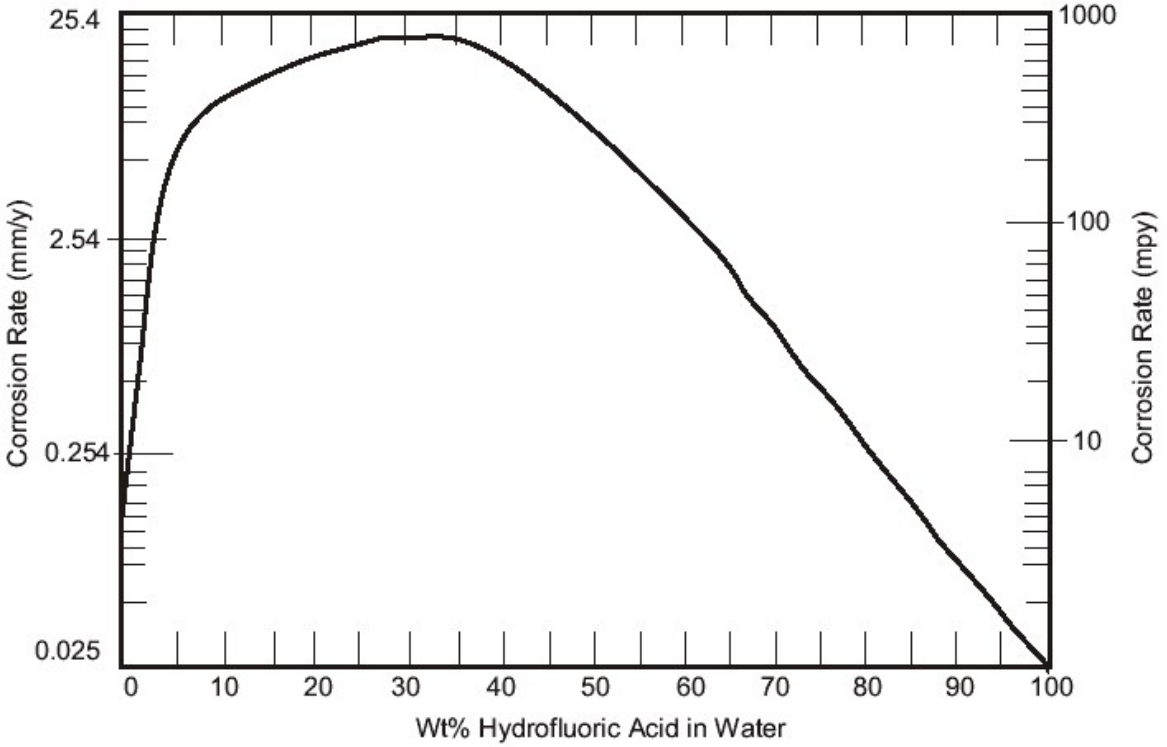


Figure 3-38-2—The corrosion rate of carbon steel at 70 °F to 100 °F (20 °C to 40 °C) based on laboratory testing and field experience at low-flow and no-flow conditions. (Reference 2)

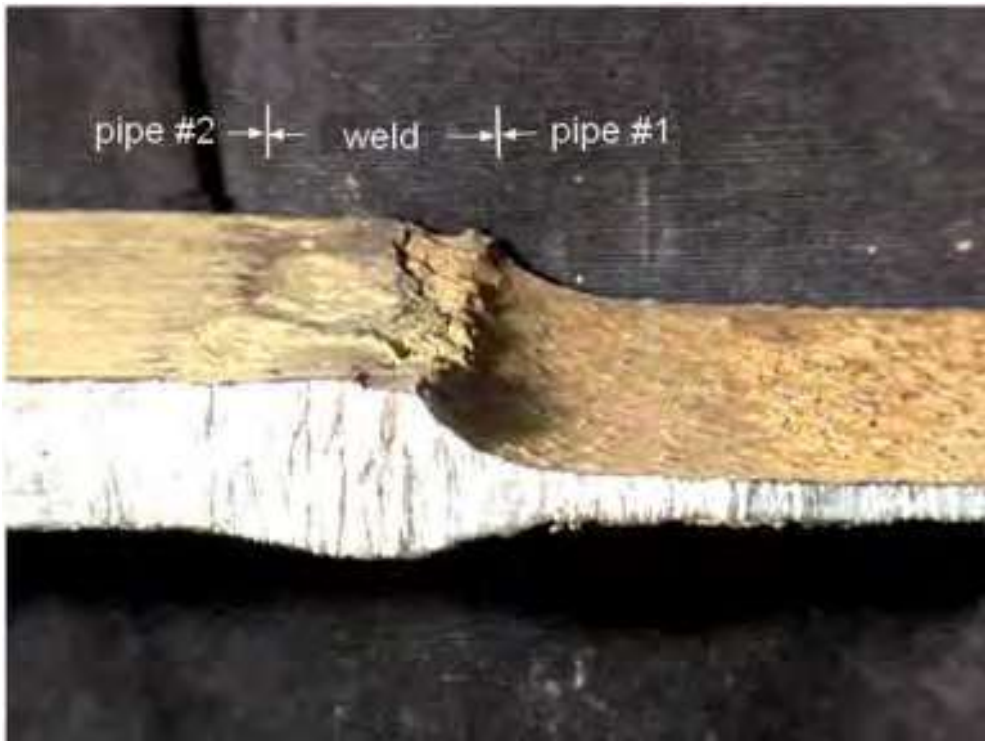


Figure 3-38-3—Cross section of a carbon steel pipe showing preferential corrosion of the pipe with high RE content on the right, as compared to the low-RE pipe section to the left of the weld. (Reference 3)

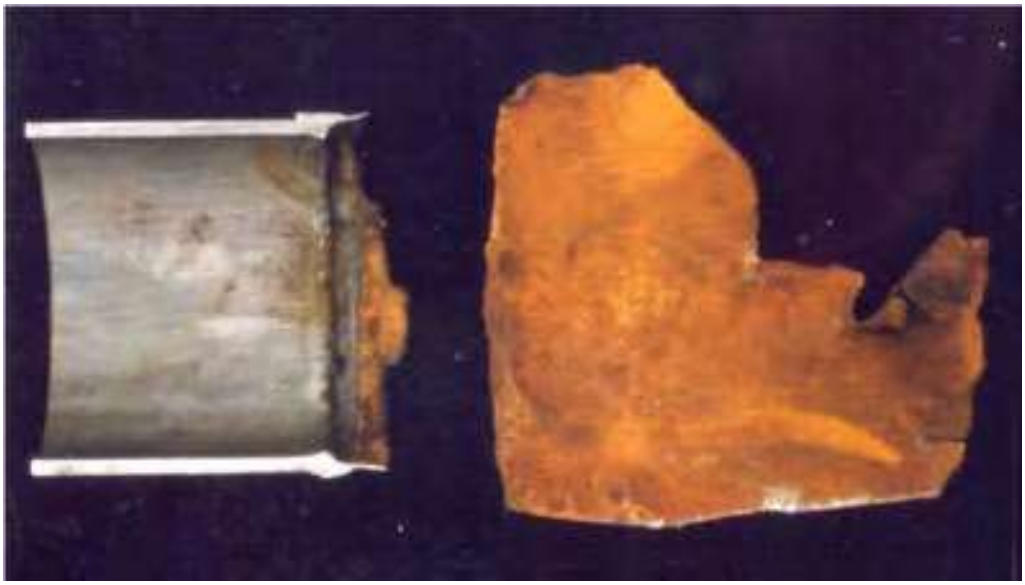


Figure 3-38-4—Ruptured NPS 3 Sch. 80 [0.216 in. (5.5 mm) wall thickness] depropanizer feed line operating < 120 °F (50 °C). RE content is as follows.
Both base metals: %C > 0.18 wt %; %Cu + %Ni < 0.15.
Weld metal: %Cu + %Ni + %Cr < 0.15.

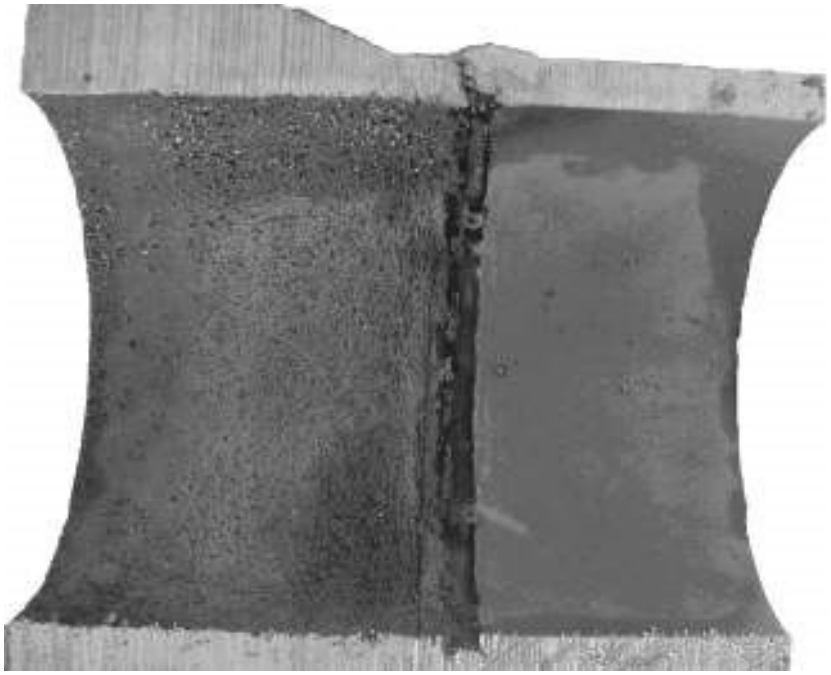


Figure 3-38-5—A cross section of a line in fresh acid service showing accelerated corrosion of the weld and base metal of the component on the left. (Reference 8)

Figure 3-38-6—Accelerated corrosion in the HAZ of a carbon steel weldment. RE content is as follows. (Reference 8)
Both base metals: %C > 0.18 wt %; %Cu + %Ni < 0.15.
Weld metal: %Cu + %Ni + %Cr < 0.15.

Figure 3-38-7—HF corrosion at a manway in HF acid storage service.

Figure 3-38-8—Internal blister caused by HF corrosion near the top of a 1.2-in.-thick carbon steel tower in an HF alkylation unit. The maximum measured dimensions of the blister were 2 ft high and 20 ft long (circumferentially). The hanging weight of an adjacent tray, which was also badly corroding, may have contributed to the location and size of the blister.

3.39 Hydrofluoric Acid Stress Corrosion Cracking of Nickel Alloys

3.39.1 Description of Damage

Surface-initiated environmental cracking of nickel alloys under the combined action of tensile stress and vapor-containing hydrofluoric acid environments, either anhydrous or wet. SCC is triggered by the presence of cupric fluoride (CuF_2), which is created by the exposure of normally protective CuF to an oxidizing agent that most commonly is oxygen in air, resulting from air ingress while onstream or during turnarounds, or as a contaminant in purge gases.

3.39.2 Affected Materials

a) Alloy 400 has a nickel content in the susceptible regime.

b) Alloy K-500 in its high-strength, strain-hardened condition is very susceptible.

c) The Ni-Cr-Mo alloys including Alloy C-22, Alloy 59, Alloy C-2000, Alloy 625, Alloy 686, and Alloy C-276, in both wrought and cast form, are sometimes susceptible to SCC in HF service when CuF_2 is present. They also are sometimes susceptible to intergranular corrosion and environmental cracking if stressed or cold worked.

3.39.3 Critical Factors

a) Oxidizing agent exposure in the presence of CuF and HF.

   1. Typically, oxygen exposure is due to air ingress with residual HF present.

   2. High levels of oxygen can also exist in in purge gases (nitrogen, fuel gas) used in acid storage, acid relief, PSV headers, etc.

b) High levels of residual stress such as in cold-worked tubing, u-bends, and as-welded welds.

c) High hardness levels, particularly in aged Alloy K-500.

3.39.4 Affected Units or Equipment

a) HF alkylation units employing nickel alloys for equipment pressure boundaries, internals, instruments, valve components (especially stems), and pump components. (Figure 3-39-1 and Figure 3-39-2)

3.39.5 Appearance or Morphology of Damage

a) Presence of CuF_2 is indicated by a green crystalline deposit. (Figure 3-39-1)

b) Annealed material will suffer intergranular corrosion and eventual cracking.

c) Cold-worked material will suffer transgranular cracking.

3.39.6 Prevention/Mitigation

a) Stress relief heat treatment will prevent SCC in cold-worked (formed components including u-bends) or welded Alloy 400.

   1. A minimum heat treatment temperature of 1300 °F (705 °C) should be used.

b) The hardness of Alloy K-500 components should be limited to a maximum of HRC 30.

c) Avoid use of Alloy 400 or Alloy K-500 for pressure boundary bolting.

d) Nickel alloy bolting for internals should be in the fully annealed form, and torque controls should be employed to avoid overtorqueing.

e) Purge/vent practices that avoid creating a vacuum and allowing air ingress should be employed.

f) Free HF should be completely removed and neutralized before opening equipment to air.

g) A maximum oxygen content of <100 ppm should be specified for purge gases.

3.39.7 Inspection and Monitoring

a) PT can be used for identifying cracks on suspected exposed components e.g. those with green crystals on the surface.

b) Purge gases should have ongoing monitoring of oxygen levels.

3.39.8 Related Mechanisms

a) CuNi Alloys (UNS C70600 and C71500) can suffer denickelification pitting corrosion when exposed to moist HF and air. (See *Dealloying*, 3.24.) Highly cold worked components, e.g. u-bends with a tight bend radius, can suffer SCC. Cold-worked u-bends should be heat treated to a minimum of 950 °F (510 °C).

b) LME (3.42) can occur in Alloy 400 due to Hg contamination.

3.39.9 References

1. NACE Publication 5A171, *Materials for Storing and Handling Commercial Grades of Aqueous Hydrofluoric Acid and Anhydrous Hydrogen Fluoride*, NACE International, Houston, TX.

2. MTI Publication MS-4, *Hydrogen Fluoride and Hydrofluoric Acid*, Materials Technology Institute of the Chemical Process Industries, St. Louis, MO.

3. *Materials of Construction Guideline for Anhydrous Hydrogen Fluoride*, Hydrogen Fluoride Industry Practices Institute (HFIPI), Washington, DC.

4. API Recommended Practice 751, *Safe Operation of Hydrofluoric Acid Alkylation Units*, American Petroleum Institute, Washington, DC.

5. H.R. Copson and C.F. Cheng, “Stress Corrosion Cracking of Monel in Hydrofluoric Acid,” *CORROSION*, Vol.12(12), 1956, pp. 71–77.

6. L. Graf and W. Wittich, Untersuchung von Sonderfällen der Spannungskorrosion bei homogenen, nicht übersättigten Mischkristallen und der hierbei auftretenden elektrochemischen Prozesse, *Werkstoffe und Korrosion/Materials and Corrosion*, Vol. 17, 1966, pp. 385–405.

7. J. D. Dobis, “The Top Ten Corrosion Issues Affecting HF Alkylation Units,” Paper No. 07570, *Corrosion/2007*, NACE International, Houston, TX.

Figure 3-39-1—HF SCC of an Alloy 400 vent line in an acid dump system. (Reference 7)

Figure 3-39-2—HF SCC of Alloy 400 instrument tubing. (Reference 7)

3.40 Hydrogen Embrittlement

3.40.1 Description of Damage

Hydrogen embrittlement (HE) is the loss in strength, ductility, and/or fracture toughness of susceptible materials due to the penetration and diffusion of atomic hydrogen. HE can lead to brittle cracking. It can occur during manufacturing, welding, or from services that charge hydrogen into the metal.

3.40.2 Affected Materials

Low-alloy steels, high-strength steels, 400 series SS, precipitation hardenable stainless steel, duplex stainless steel, and some high-strength nickel-based alloys. Carbon steel can suffer HE if hardened by cold work or welding. Typically, a steel has to have hardness greater than Rockwell hardness number (HRC) 22 to be susceptible to HE cracking in the most severe environments. Higher strength/hardness can be tolerated in milder environments. (For the purposes of this section, blistering and HIC are not considered examples of HE. See 3.67, *Wet H_2S Damage*.)

3.40.3 Critical Factors

a) The following five conditions must be satisfied.

1. The material must be susceptible.
2. Hydrogen must be present at a critical concentration within the material.
3. The strength/hardness level must be high enough and the microstructure must be susceptible to HE.
4. A stress above the threshold for HE must be present from residual stresses and/or applied stresses.
5. The temperature must be in the embrittling and cracking range. HE generally diminishes with increasing or decreasing temperature away from ambient.

b) The hydrogen can come from the following.

1. Welding—If wet electrodes or electrodes with a high moisture content flux are used, hydrogen can be charged into the material. Cracking in a susceptible material from this cause is often called delayed cracking or underbead cracking.
2. Corrosion Reactions—Most aqueous corrosion reactions produce hydrogen. Wet H_2S services and HF acid services in which atomic hydrogen diffuses into the metal as the result of the corrosion reaction are two of the most severe and common examples. (See *Wet H_2S Damage*, 3.67, and *Hydrogen Stress Cracking in Hydrofluoric Acid*, 3.41.) Sulfur and arsenic act as atomic hydrogen recombination poisons in wet H_2S and HF acid environments, respectively, that inhibit the reaction of atomic hydrogen to form H_2 gas, thus enabling a higher percentage of hydrogen atoms to diffuse into the metal. Cyanide can also promote hydrogen charging by forming a complex with the surface films rendering them less protective. This in turn results in increased corrosion with associated increases in atomic hydrogen production. In very high strength, highly susceptible steels, the corrosion reaction alone, without the need for a recombination poison, can lead to HE cracking.
3. Service in high-temperature [>400 °F (205 °C)] hydrogen gas atmospheres. Molecular hydrogen dissociates to form atomic hydrogen that can diffuse into the metal.
4. Cleaning and pickling in acid solutions.
5. Manufacturing—Melting practices or manufacturing processes, particularly where susceptible components are plated, e.g. high-strength bolts plated with cadmium, can lead to HE cracking. This is sometimes called hydrogen flaking.

6. Cathodic Protection—Hydrogen is formed on the surface of the protected metal, which can lead to HE cracking if the metal is susceptible.

c) The effect is generally most pronounced at ambient temperatures, decreases rapidly above 150 °F (65 °C), and effectively disappears above about 300 °F (150 °C). The temperature above which it is no longer a practical concern in a given circumstance varies depending on the susceptibility of the material and the hydrogen charging environment.

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) Stress to cause cracking can result from cooling during manufacture or from PWHT temperatures, residual stresses from welding, or applied loads.

h) Thick wall components can be more vulnerable due to increased thermal stress during cool-down from operating temperatures, high restraint and potentially high stress concentrations at flaws or cracks, and because they take longer for hydrogen to diffuse out.

i) In general, as strength increases, susceptibility to HE increases. Certain microstructures, such as untempered martensite, are more susceptible at the same strength level than tempered martensite. Carbon steel that is severely hydrogen charged will have lower fracture toughness than with no hydrogen.

j) HE is reversible as long as cracking has not occurred. The hydrogen can be baked out at elevated temperature [400 °F (205 °C) or higher, typically around 600 °F (315 °C)].

3.40.4 Affected Units or Equipment

a) Cr-Mo reactors, drums, exchanger shells, and piping in hydroprocessing units and catalytic reforming units can be susceptible to cracking if the weld HAZ hardness exceeds Brinell hardness number (HB) 225.

b) Storage spheres are often made of higher-strength steels (>70 ksi specified minimum tensile strength) than common pressure vessel steels and are therefore more susceptible than most other refinery equipment if not stress relieved.

c) Bolts and springs made of high-strength steel are very prone to HE cracking. Components that have a tensile strength above 150 ksi can absorb hydrogen during electroplating and crack prior to being put in service.

d) Other services where HE is a concern include where susceptible materials such as high-strength valve components, instrument components, and similar are exposed to wet H_2S in FCC, hydroprocessing, amine, SW, and other H_2S-containing services, as well as HF in alkylation units. For these services, equipment manufactured using HE-resistant materials for the potentially susceptible components is typically selected, with the materials meeting the requirements of, e.g. NACE MR0103/ISO 17945. (See *Wet H_2S Damage*, 3.67, and *Hydrogen Stress Cracking in Hydrofluoric Acid*, 3.41.)

e) Carbon steels normally used for vessels, piping, and other equipment in most refining applications have low strength/hardness and are usually not susceptible to HE as long as typical welding procedures and precautions regarding controlling the moisture in welding consumables are followed.

3.40.5 Appearance or Morphology of Damage

a) HE by itself is not visible. It only appears when cracking occurs.

b) Cracking resulting from HE can initiate subsurface but in most cases is surface breaking. (Figure 3-40-1 and Figure 3-40-2)

c) HE cracking occurs at locations of high residual or tri-axial stresses (notches, restraint) and where the hardness and microstructure are conducive, such as in weld HAZs.

d) On a macro-scale, there is typically little evidence of deformation. Cracking will appear to be brittle, with visible fracture surfaces having a brittle appearance. On a microscale, the material will contain less ductile fracture surface but must often be compared to a fracture without the presence of hydrogen.

e) Under metallographic examination, cracking is typically branched. In higher-strength steels, cracking is often intergranular. (Figure 3-40-1)

3.40.6 Prevention/Mitigation

a) Depending on the source of the hydrogen, choose an alloy composition, fabrication/heat treatment method, and hardness limit suitable for the intended service.

b) Control the hardness of hardenable steels and PWHT to reduce hardness and temper residual stresses.

c) During welding, use dry, low-hydrogen electrodes and preheating methods.

d) If hydrogen diffused into the metal during welding is a concern, an elevated temperature bake-out [400 °F (205 °C) or higher, typically around 600 °F (315 °C)] may be required to drive the hydrogen out prior to cooling to ambient temperature.

e) If hydrogen is expected to have diffused into the metal during operation, a similar elevated temperature bake-out [400 °F (205 °C) or higher, typically around 600 °F (315 °C)] may be required to drive out the hydrogen out prior to welding for maintenance or repair.

f) Heavy wall equipment in hot hydrogen service typically requires controlled shutdown and start-up procedures to control the pressurization sequence as a function of temperature.

g) In corrosive aqueous services, a protective lining, cladding, or weld overlay can be applied to prevent the surface hydrogen reactions.

h) Avoid the use of cadmium or other plating on high-strength bolts.

3.40.7 Inspection and Monitoring

a) PT, MT, or WFMT can be used for surface cracking inspection.

b) Angle beam (e.g. SWUT or PAUT) may also be useful in finding as well as sizing HE cracks.

c) RT often is not sufficiently sensitive to detect HE cracks.

d) VT is not reliable for finding HE cracks.

e) If the source of hydrogen is a low-temperature aqueous environment, hydrogen flux can be monitored using specialized instruments.

3.40.8 Related Mechanisms

Also known as underbead cracking, delayed cracking, hydrogen-assisted cracking, and hydrogen flaking, SSC (covered in 3.67) and hydrogen stress cracking in HF acid (3.41) are closely related forms of HE.

3.40.9 References

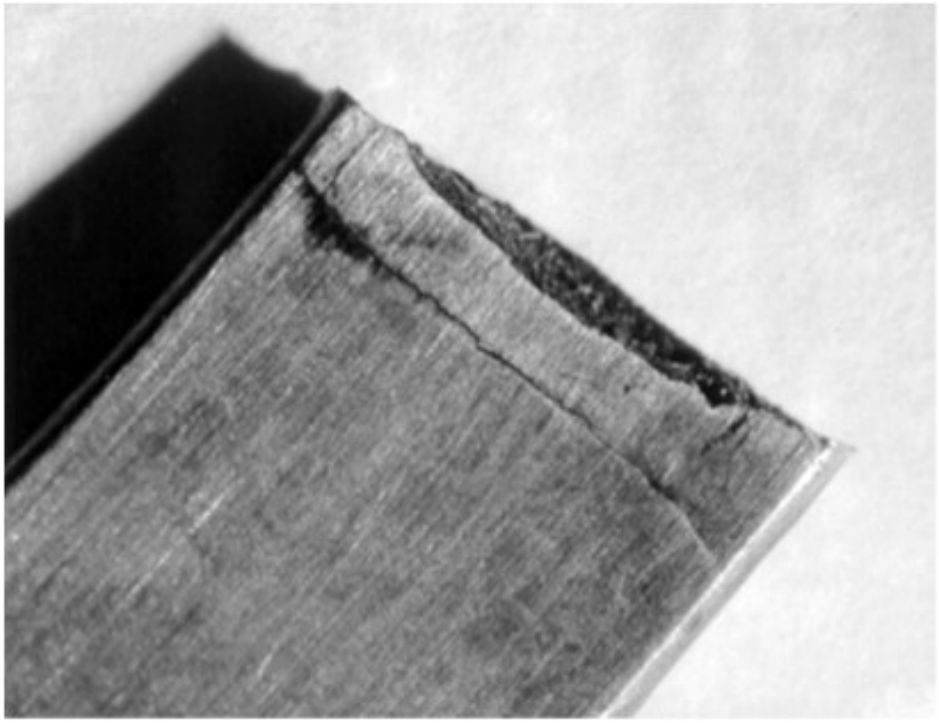
1. W.E. Erwin and J.G. Kerr, *The Use of Quenched and Tempered 2¼Cr-1Mo Steel for Thick Wall Reactor Vessels in Petroleum Refinery Processes: An Interpretive Review of 25 Years of Research and Application*, WRC Bulletin 275, Welding Research Council, Shaker Heights, OH.

2. R.S. Treseder, "Guarding Against Hydrogen Embrittlement," *Chemical Engineering Magazine*, Chemical Week Publishing, June 1981.

3. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.

4. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, pp. 120–121.

5. NACE MR0103/ISO 17945, *Petroleum, petrochemical and natural gas industries—Metallic materials resistant to sulfide stress cracking in corrosive petroleum refining environments*, NACE International, Houston, TX.

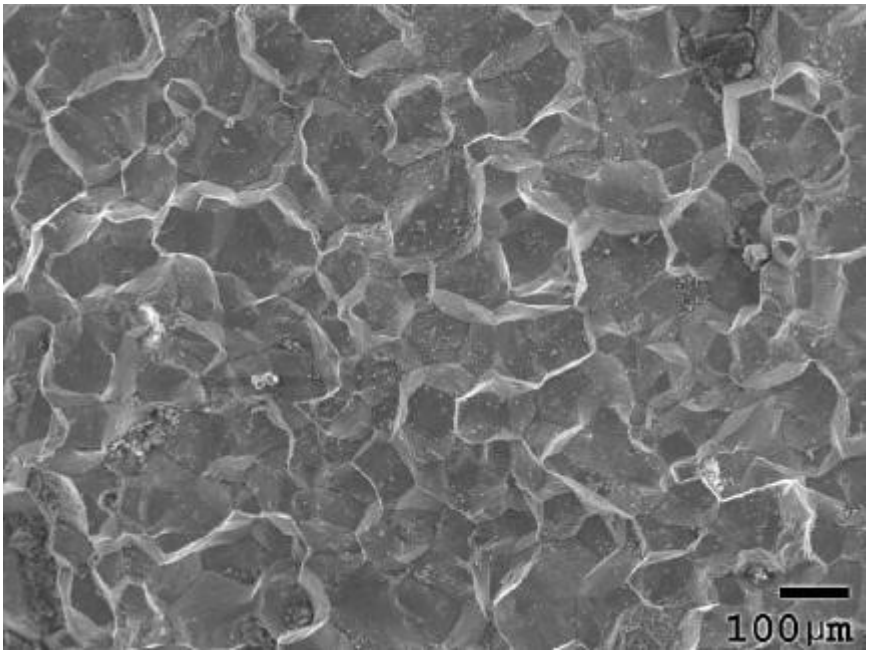


(a)

(b)

Figure 3-40-1—(a) Cracking due to HE of a high-strength steel tube. (b) Intergranular crack emanating from surface in the tube.

(a)



(b)

Figure 3-40-2—(a) HE of a martensitic stainless steel pump component. (b) High-magnification fractograph of the fracture surface showing intergranular nature of the cracking.

3.41 Hydrogen Stress Cracking in Hydrofluoric Acid

3.41.1 Description of Damage

Hydrogen stress cracking is a form of environmental cracking that can occur in high-strength low-alloy (HSLA) steels and carbon steels with highly localized zones of high hardness in the weld metal and HAZ, as the result of exposure to aqueous HF acid environments.

3.41.2 Affected Materials

Carbon steel and low-alloy steels.

3.41.3 Critical Factors

a) Steel hardness, strength, and stress are the critical materials factors.

b) Susceptibility increases with increasing hardness. Steels with hardness levels above HRC 22 (HB 237) are highly susceptible. Time-to-failure decreases as the hardness, which directly correlates to strength level, increases, i.e. higher-strength steels are more susceptible.

c) Under high levels of applied or residual tensile stress (from cold-forming or welding), embrittlement resulting from the hydrogen charged into the steel by the corrosion reaction in HF [i.e. hydrogen embrittlement (see 3.40)] results in cracking of susceptible steels.

d) Cracking may occur very rapidly, within hours after exposure to the HF environment, or considerable time may pass before cracking initiates.

e) In low-alloy steels, but also potentially in carbon steel, particularly with low-heat-input welds, hard microstructures may arise in the weld and HAZs as the result of high hardenability and inadequate heat treatment.

3.41.4 Affected Units or Equipment

a) All piping and equipment exposed to HF acid at any concentration with hardness levels above the recommended limit are subject to hydrogen stress cracking.

b) HSLA steels used for components such as ASTM A193-B7 bolts as well as valve and compressor parts are susceptible.

c) ASTM A193-B7M bolts can be susceptible if overtorqued.

3.41.5 Appearance or Morphology of Damage

a) This mode of cracking can only be confirmed by metallographic examination. The cracking will be primarily transgranular in carbon steel. In high-strength steel, it may be intergranular.

b) Cracks are surface breaking and are usually associated with weldments.

3.41.6 Prevention/Mitigation

a) Weld procedure qualification, chemistry controls, and PWHT are the methods used to avoid high-hardness HAZs.

b) Welding controls are employed to minimize the potential for hard welds and HAZs in carbon steel and low-alloy steels. (See e.g. NACE SP0472.) Typical options used in HF service include the following.

   1. Use of carbon steels with carbon equivalent (CE) and RE chemistry controls. CE is defined as:

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

   2. RE controls are described in *Hydrofluoric Acid Corrosion*, 3.38.3 k).

   3. PWHT, which is beneficial in reducing the hardness and residual stresses that contribute to hydrogen stress cracking.

   4. Use of exempt welding process/filler metal combinations.

   5. Production weld metal hardness testing to ensure hardness < HB 200.

c) ASTM A193 grade B7M bolts are softer and lower strength than B7 bolts and are considered resistant to cracking.

d) Alloy cladding or nonmetallic coatings that provide an effective barrier and protect the surface of the steel from corrosion and hydrogen permeation will prevent cracking.

e) Alloy 400 is not susceptible to this form of cracking but may be susceptible to SCC, particularly in the non-stress-relieved condition. (See 3.39.) DMW between Alloy 400 and carbon steel may also be susceptible to cracking when exposed to HF. (See 3.27.)

3.41.7 Inspection and Monitoring

a) Surface-breaking cracks can be found by PT, MT, or WFMT.

b) Angle beam UT (SWUT or PAUT) may also be useful for finding or determining the depth of cracks. Straight beam UT can identify cracked bolts.

c) ACFM can be used in lieu of WFMT for crack detection; however, it is highly operator dependent.

d) Hardness testing of weld metal and bolting is the best method to determine the susceptibility of suspect material.

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

3.41.8 Related Mechanisms

This is the same mechanism (i.e. HE, 3.40) that is responsible for SSC in wet H_2S environments except that HF acid corrosion is generating the hydrogen. Blistering, HIC, and SOHIC damage in HF acid is similar to that found in wet H_2S. (See 3.67.) See also *Hydrofluoric Acid Stress Corrosion Cracking of Nickel Alloys*, 3.39.

3.41.9 References

1. J.D. Dobis, D.R. Clarida and J.P. Richert, “Survey Reveals Nature of Corrosion in HF Alkylation Units,” *Oil and Gas Journal*, Vol. 93, No. 10, March 6, 1995, pp. 63–68.

2. J. Gutzeit, R.D. Merrick, and L.R. Scharfstein, “Corrosion in Petroleum Refining and Petrochemical Operations,” *Metals Handbook*, Volume 13, ASM International, Materials Park, OH, 1987, pp. 1262–1287.

3. NACE SP0472, *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*, NACE International, Houston, TX.

3.42 Liquid Metal Embrittlement

3.42.1 Description of Damage

Liquid metal embrittlement (LME) is a form of cracking that results when certain molten or liquid metals (the embrittler) come in contact with specific alloys. Cracking can be very sudden and brittle in nature. Laboratory experiments have demonstrated that, for some metal/embrittler couples, embrittlement can also occur at temperatures below the embrittler melting point (solid metal embrittlement).

3.42.2 Affected Materials

Many commonly used materials including carbon steel, low-alloy steels, high-strength steels, 300 series SS, nickel alloys, copper alloys, aluminum alloys, and titanium alloys.

3.42.3 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. Combinations of industrial significance are shown in Table 3-42-1.

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) The embrittler can be external to the metal, such as zinc on the surface of stainless steel, or the embrittler can be internal to the metal, such as the lead in a leaded free-machining steel.

d) Tensile stress contributes to high 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.

e) In cases where embrittlement is severe, fracture occurs at virtually zero percent strain.

f) A susceptible metal in contact with or contaminated with a low-melting metal will not crack while at low temperatures but may crack later when the temperature rises above the melting temperature of the low-melting alloy.

3.42.4 Affected Units or Equipment

a) In refining, LME is relevant and of most concern after a fire, after failure of an instrument containing mercury (Hg) that leaks into or onto equipment, or where the incoming crude contains mercury.

b) During a fire, molten metals may drip onto or contact a susceptible metal. Examples include melted zinc galvanizing, cadmium electrical housings, cadmium plated bolts, studs, or nuts, tin or lead from solders, and melted copper components.

    1. Probably the most relevant example in refining is 300 series SS piping or vessels near or in contact with (or previously rubbed against) galvanized steel where the zinc melts during a subsequent fire and cracks the stainless steel. (Figure 3-42-1 and Figure 3-42-2)

c) Failure of process instruments that utilize mercury can introduce the liquid metal into refinery streams. (Figure 3-42-3)

d) 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.

e) LME of aluminum components has occurred in LNG facilities and cryogenic gas plant components due to condensation of liquid mercury.

3.42.5 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.

3.42.6 Prevention/Mitigation

a) LME can only be prevented by protecting metal surfaces 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 inorganic zinc and other zinc-containing coatings.

b) Once cracking from LME has initiated, grinding out the affected area is unlikely to be an acceptable or practical fix.

3.42.7 Inspection and Monitoring

a) Cracks are often visually apparent.

b) Cracks in carbon and low-alloy steels and other ferritic materials can be detected with MT or WFMT examination. For 300 series SS, nickel-based alloys, and other nonmagnetic materials, PT examination can be used.

c) Inspection for LME after a fire should be focused where molten metal has dripped on equipment and solidified.

d) Because of the high density of mercury, RT has been used to locate deposits inside equipment, piping, and tubes. A boroscope can also be used to visually detect liquid mercury inside equipment.

3.42.8 Related Mechanisms

LME is also referred to as liquid metal cracking. Nickel alloys are susceptible to a similar mechanism caused by the nickel-nickel sulfide eutectic that forms at 1157 °F (625 °C).

3.42.9 References

1. *ASM Handbook—Failure Analysis and Prevention*, Volume 11, ASM International, Materials Park, OH.

2. C.P. Dillon, *Corrosion Control in the Chemical Process Industries*, Materials Technology Institute (printed by NACE), MTI Publication No 45, Second Edition, St. Louis, MO, 1994, pp. 84–85.

Table 3-42-1—Some LME Couples Susceptible to Embrittlement (See Note)

Susceptible Alloy	Molten Metal
Carbon steel	Lead, cadmium
Low-alloy steel and high-strength steels	Lead, cadmium
300 series SS	Zinc, copper, high-copper brazing alloys
Copper alloys	Mercury, lead, lead-tin solders
Alloy 400	Mercury
Nickel alloys	Mercury, lead
Aluminum alloys	Mercury, tin
Titanium	Mercury

NOTE Laboratory testing has shown that there are other molten metals that will embrittle the susceptible alloys listed. However, the information in Table 3-34-1 is limited to those molten metals known to be of significance to the refining and petrochemical industries.

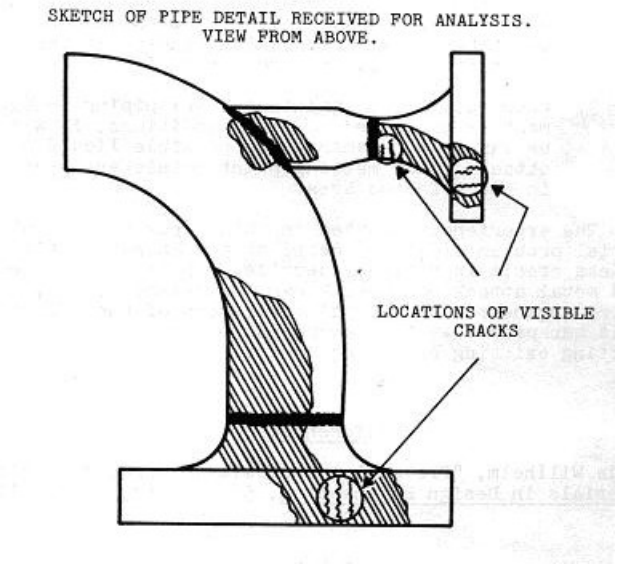


Figure 3-42-1—Sketch of a stainless steel elbow that suffered liquid metal embrittlement as the result of dripping molten zinc during a fire.

Figure 3-42-2—Photomicrograph of a section of the elbow in Figure 3-40-1, illustrating the intergranular nature of zinc-filled cracks in stainless steel.

Figure 3-42-3—LME of Monel caused by mercury in an FCC gas plant overhead drum.

3.43 Mechanical Fatigue (Including Vibration-induced Fatigue)

3.43.1 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, e.g. from dynamic loading due to vibration, water hammer, or unstable fluid flow, often resulting in sudden, unexpected thru-wall cracking.

b) These stresses can arise from either mechanical loading or thermal cycling and are typically well below the yield strength of the material. This section focuses on mechanical loading, while the effects of thermal cycling are covered in 3.64 on thermal fatigue.

3.43.2 Affected Materials

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

3.43.3 Critical Factors

a) Geometry, stress level, number of cycles, and material properties (strength, hardness, microstructure) are predominant factors in determining the fatigue resistance of a component. The amplitude and frequency of vibrations (related to stress level and number of cycles) in vibrating equipment such as piping are also critical factors. There is a high likelihood of cracking when the input vibrational load is synchronous or nearly synchronizes with the natural or harmonic frequency of the component.

b) Design Factors—Fatigue cracks usually initiate on the surface at notches or stress risers under cyclic loading. For this reason, design of a component is the most important factor in determining a component's resistance to fatigue cracking. Common surface features that can lead to the initiation of fatigue cracks, because they act as stress concentrations, include:

1. key holes on drive shafts of rotating equipment,
2. mechanical notches (sharp corners or groves),
3. weld joint flaws and/or mismatches,
4. tool markings,
5. grinding marks,
6. lips on drilled holes,
7. thread root notches, and
8. corrosion.

In vibrating or shaking equipment, especially piping, a lack of or improperly placed support or stiffening can lead to cracks initiating at the types of stress risers or notches listed above. The normal toe or edge of a properly made, *Code*-acceptable weld can provide the stress concentration to initiate a fatigue crack in badly vibrating or shaking equipment. Often the cracks will form at the location(s) where the vibrating or shaking equipment is fixed and prevented from moving with the adjacent component. This situation most often needs to be addressed by reducing the amount of vibration or shaking.

c) Metallurgical issues and microstructure.

1. Some materials such as titanium, carbon steel, and low-alloy steel have an "endurance limit." In such cases, the number of cycles to fatigue fracture increases with decreasing stress amplitude until a stress

amplitude endurance limit is reached below which fatigue cracking will not occur, regardless of the number of cycles.

2. For alloys with endurance limits, there is a correlation between ultimate tensile strength (UTS) and the minimum stress amplitude necessary to initiate fatigue cracking, i.e. the endurance limit. The ratio of endurance limit to UTS is typically between 0.4 and 0.5.

3. 300 series SS, 400 series SS, aluminum, and most other non-ferrous alloys have a fatigue characteristic that does not exhibit an endurance limit. This means that fatigue fracture can be achieved under cyclic loading eventually, given enough cycles, regardless of stress amplitude. Maximum cyclic stress amplitude for design is selected by determining the cyclic stress necessary to cause fracture in the number of cycles the component needs to withstand in its lifetime. This is typically 10^6 to 10^7 cycles.

4. The endurance limit described in Item 1 above primarily applies to smooth bars and similar configurations as might be found in a pump shaft. For welded components, such as piping or other situations where inherent discontinuities, flaws, or other high stress concentrations exist, the crack initiation portion of fatigue life is essentially eliminated, leaving only the crack growth portion. This situation effectively eliminates the existence of the endurance limit. Thus, the concept of the endurance limit generally cannot be taken advantage of with vibrating or shaking equipment.

5. 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.

6. Heat treatment can have an effect on 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.

3.43.4 Affected Units or Equipment

a) Socket welds and small-bore piping (e.g. bypass lines, minimum flow loops) associated with or near pumps, compressors, or other rotating or reciprocating equipment that are not properly gusseted and supported.

b) Small branch connections with unsupported valves or controllers that may see vibration from adjacent equipment and/or wind. For small components, resonance can also produce a cyclic load and should be taken into consideration during design and reviewed for potential problems after installation.

c) Safety-relief valves that are subject to chatter, premature pop-off, fretting, and failure to operate properly.

d) High-pressure-drop control valves or steam-reducing stations that can cause serious vibration problems in connected piping.

e) Rotating shafts on centrifugal pumps and compressors that have stress concentrations due to changes in radii and keyways.

f) Heat exchanger tubes that may be susceptible to vortex shedding.

g) Pressure swing absorber vessels in hydrogen purification units.

h) Transient conditions (such as start-ups, shutdowns, upsets, etc.) can create intermittent, but severe, vibrating conditions.

3.43.5 Appearance or Morphology of Damage

a) Damage is usually in the form of a crack emanating from a point of high stress concentration or discontinuity such as thread, a weld (Figure 3-43-1 to Figure 3-43-4), or the corner of a keyway in a shaft.

b) 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 3-43-5 to Figure 3-43-8). 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 tensile overload occurs.

c) Cracks nucleating from a surface stress concentration or defect will typically result in a single “clam shell” fingerprint. (Figure 3-43-8)

d) Cracks resulting from cyclical overstress of a component without one significant, isolated stress concentration point will typically result in a fatigue failure with multiple points of nucleation and hence multiple “clam shell” fingerprints. These multiple nucleation sites, often called “ratchet markings,” are the result of microscopic yielding that occurs when the component is momentarily cycled above its yield strength. (Figure 3-43-9)

3.43.6 Prevention/Mitigation

a) Piping and other fixed equipment.

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

2. Fatigue cracking in piping can usually be eliminated or reduced through proper design and the use of properly placed support and vibration dampening equipment. Material upgrades are not usually a solution.

3. Install gussets or stiffeners on small-bore connections so that they cannot move independently of the larger pipe or other component to which they are connected. Eliminate unnecessary connections.

4. Vortex shedding can be minimized at the outlet of control valves and safety valves through proper side branch sizing and flow stabilization techniques.

5. 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.

6. Assure good fit-up and smooth transitions for welds. Employ a gradual bore taper on the thicker component when transitioning between different pipe schedules.

7. Minimize weld defects as these can accelerate fatigue cracking.

8. Minimize grinding marks, nicks, and gouges on the surface of components subject to cyclic loading.

9. Use low-stress stamps and marking tools.

b) Rotating equipment.

1. Allow for a generous radius along edges and corners, particularly in shaft keyways.

2. Remove any burrs or lips caused by machining.

3. Although fatigue cracking problems are generally addressed by design and fabrication improvements, ensure that the metal selected has fatigue life sufficient for its intended cyclic service.

c) API 579-1/ASME FFS-1 contains useful information related to determining critical fatigue crack sizes and assessing crack growth rates.

3.43.7 Inspection and Monitoring

In high cycle fatigue, the time required for a crack to initiate or grow sufficiently to be identifiable by NDE

methods can be a majority of the fatigue life, making detection before cracking and failure difficult. For this reason, it is normally impractical to rely on NDE methods for routine, global inspection of fixed equipment to avoid fatigue cracking failures. Frequent NDE in a focused program aimed at a specific, known problem area can be used for finding cracks before failure, but this is not normally considered an effective, long-term approach to managing the problem.

a) PT can be used to detect cracks open to the surface.

b) MT (including WFMT) can be used to detect cracks open to the surface or near the surface.

c) Angle beam (SWUT and PAUT) can be used to detect fatigue cracks at known or suspected areas of concern, e.g. at stress concentrations and welded connections, and where cracking is internal, i.e. initiating on the ID surface and not visible from the outside. In some situations, e.g. with very thick components, compression wave UT may be needed.

d) Compression wave UT can detect cracking in bolts.

e) Vibration monitoring of rotating equipment may provide online detection of conditions that can result in shaft failures due to out of balance conditions.

f) Piping oscillation, vibration, or water hammer, especially involving small-bore components that are not adequately supported, is often visually apparent. Focus on weld joints and locations where the pipe is fixed and prevented from moving. Pipe vibrations can be measured using special monitoring equipment.

g) Pipe supports and spring hangers should be checked on a regular schedule.

h) Audible sounds of vibration emanating from components such as control valves can be an indication of conditions capable of causing fatigue cracks.

i) Damaged insulation jacketing may indicate excessive vibration.

3.43.8 Related Mechanisms

Thermal fatigue (3.64) and corrosion fatigue (3.21).

3.43.9 References

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

2. ASTM STP1428, *Thermomechanical Fatigue Behavior of Materials*, American Society for Testing and Materials, West Conshohocken, PA.

3. ASTM MNL41, *Fracture and Fatigue Control in Structures: Applications of Fracture Mechanics*, ASM International, Materials Park, OH, 1995.

4. “Environmental Effects on Components: Commentary for ASME Section III,” EPRI NP-5775, Project 1757-61, Final Report, EPRI, 1998.

5. API Recommended Practice 581, *Risk-Based Inspection Technology*, American Petroleum Institute, Washington, DC, Second Edition, 2008.

6. API 579-1/ASME FFS-1, *Fitness-For-Service*, American Petroleum Institute, Washington, DC.

Figure 3-43-1—Vibration induced fatigue of a 1-in. socket weld flange in a thermal relief system shortly after start-up.

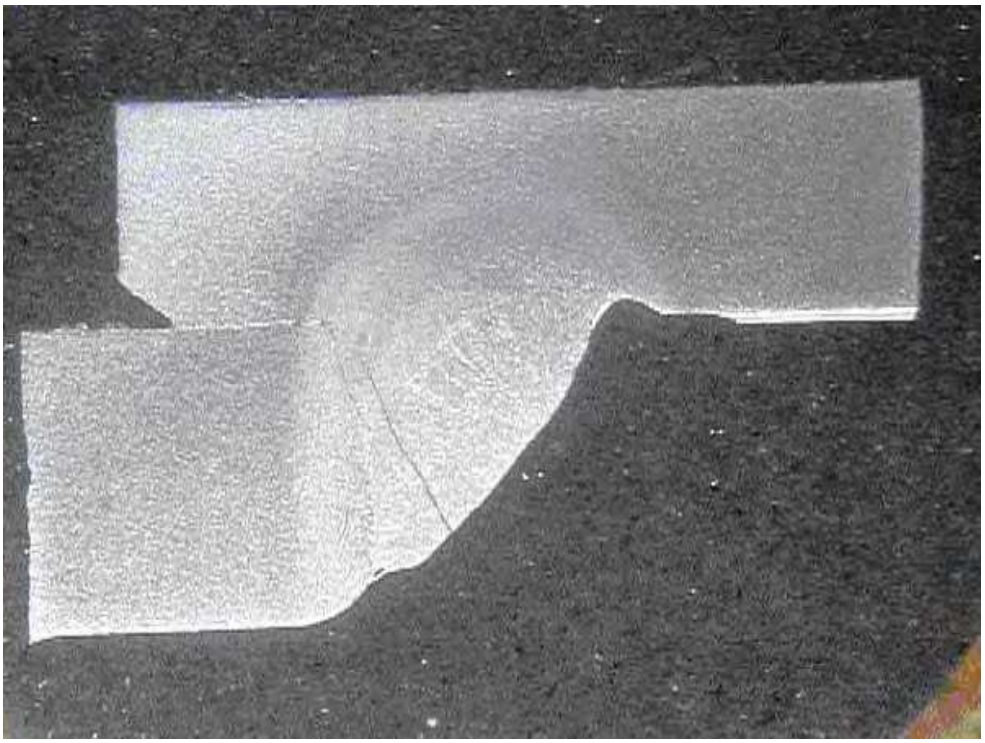


Figure 3-43-2—Cross-sectional view of the crack in the socket weld in Figure 3-41-1.

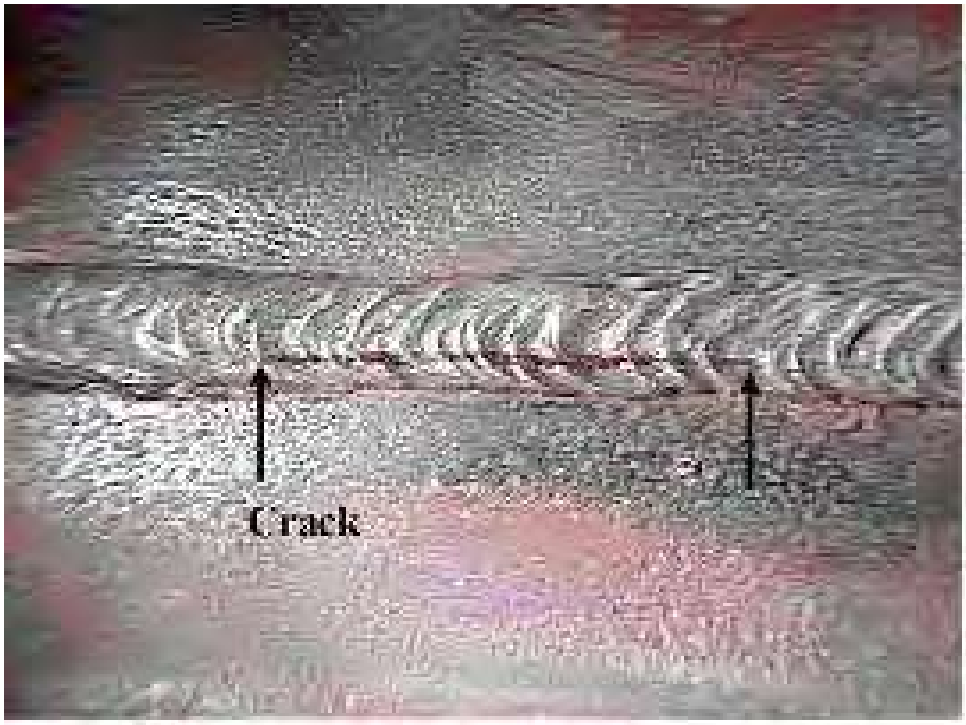


Figure 3-43-3—Fatigue crack in a 16-in. pipe-to-elbow weld in the fill line of crude oil storage tank after 50 years in service.

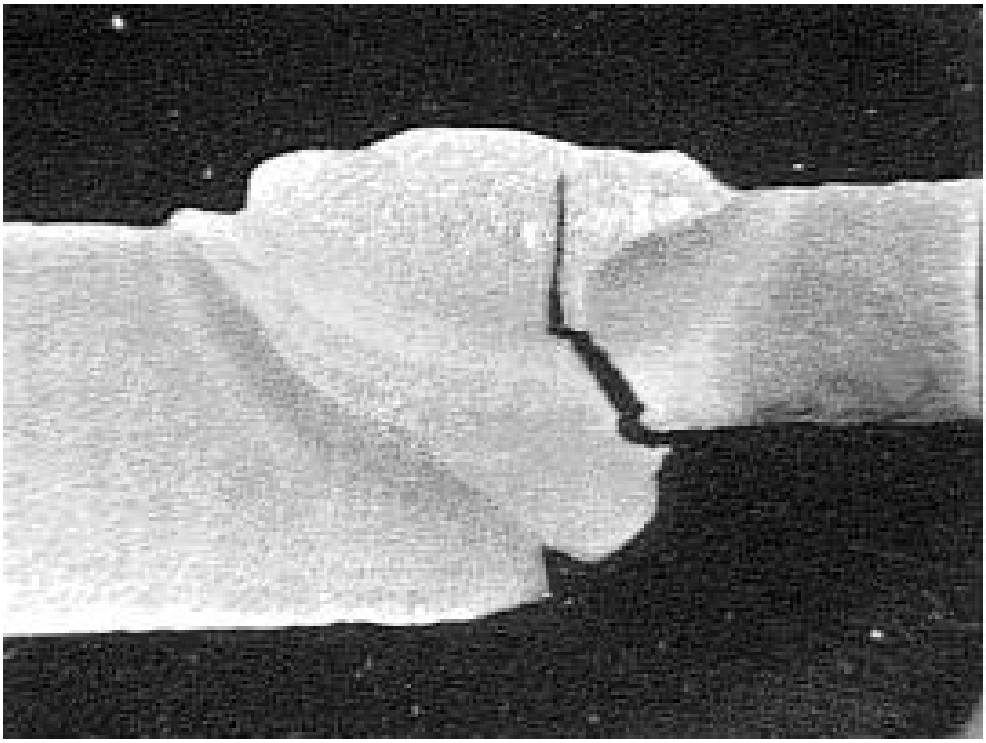


Figure 3-43-4—A cross section through the weld showing the crack location.

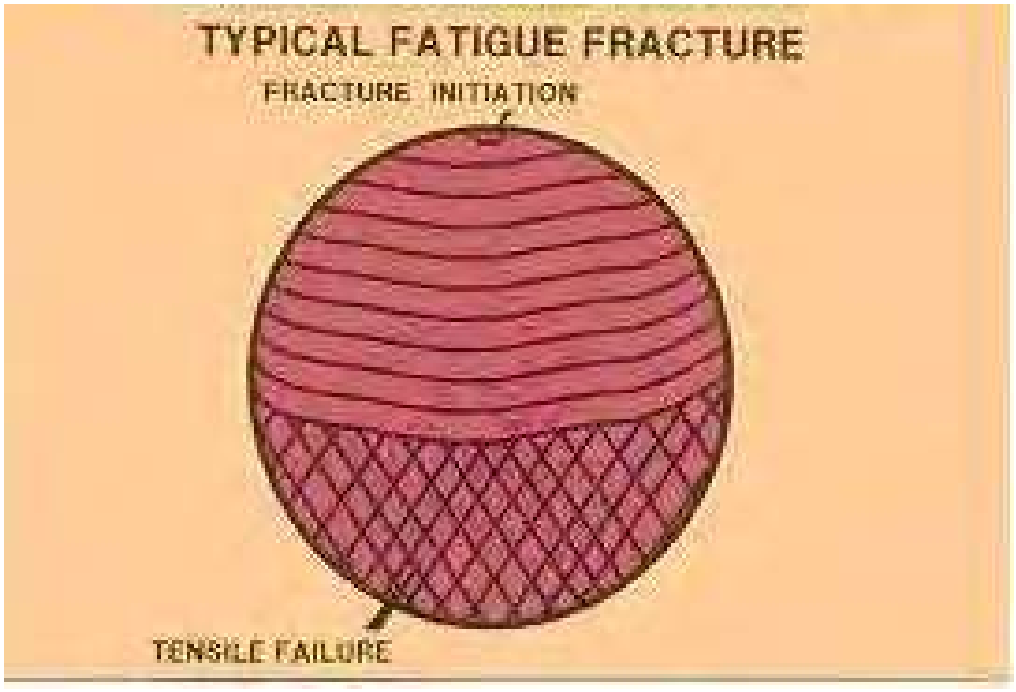


Figure 3-43-5—Schematic of a fatigue fracture surface showing "beach marks."

Figure 3-43-6—Compressor rod fracture surface showing "beach marks."

Figure 3-43-7—Higher-magnification view of Figure 3-41-6 above showing "beach marks."

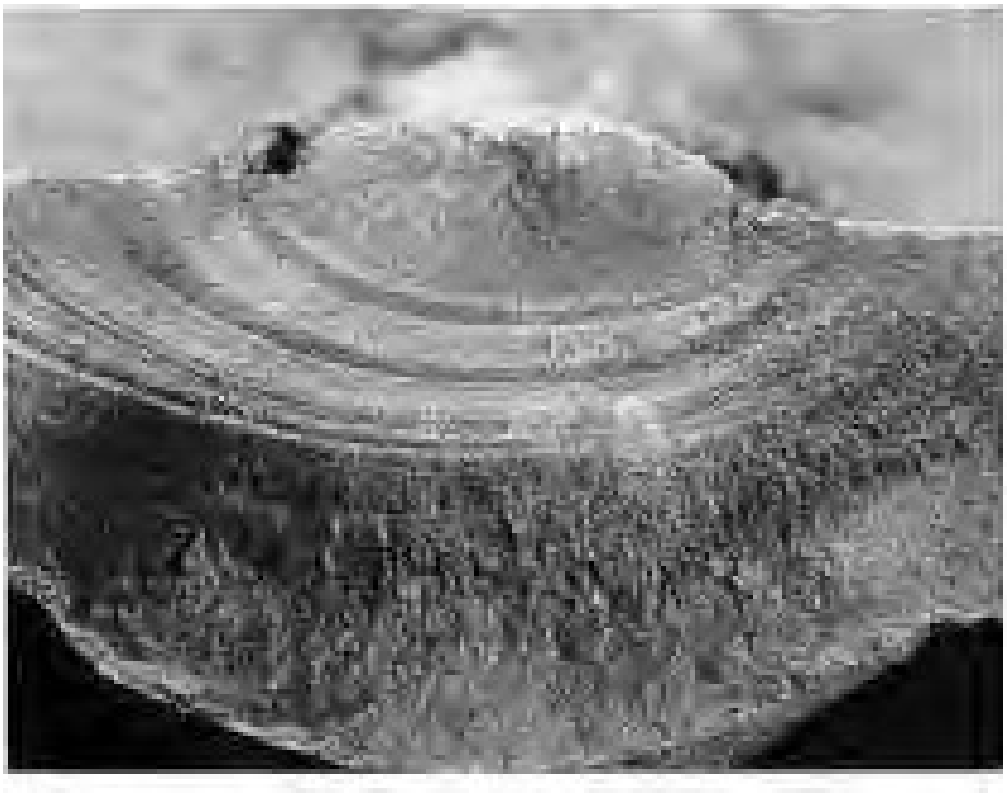


Figure 3-43-8—Fatigue fracture surface of a carbon steel pipe.

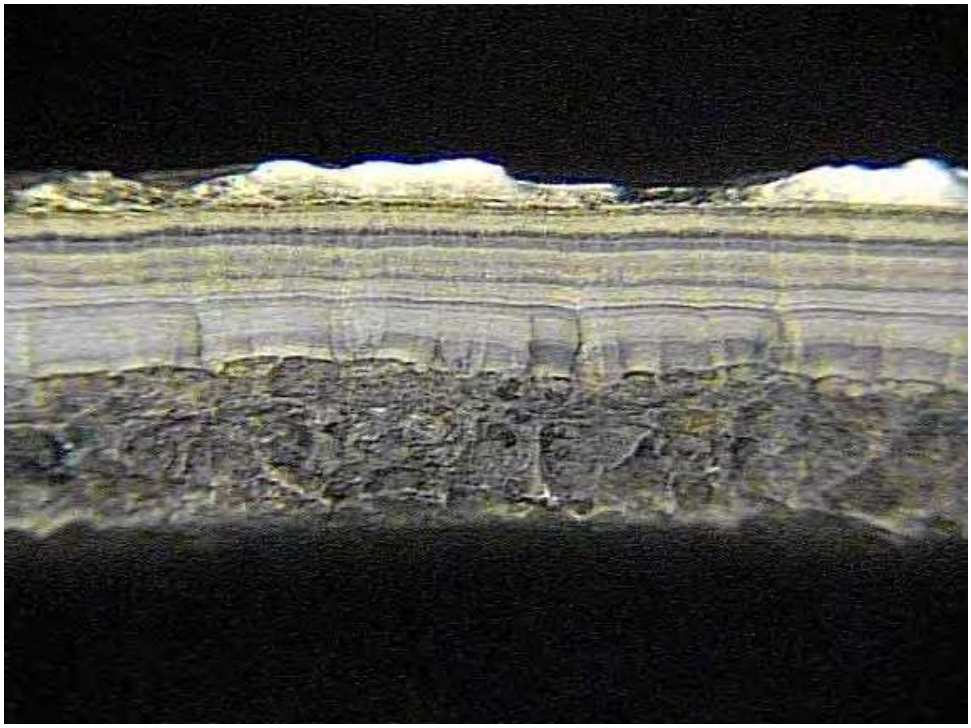


Figure 3-43-9—The surface of the fracture face of the crack shown in Figure 3-41-3 and Figure 3-41-4.

3.44 Metal Dusting

3.44.1 Description of Damage

a) Metal dusting results in accelerated localized pitting that occurs in process streams containing carbon and oxygen. Pits form on the surface and may contain carbon soot and metal dust particles. Typically, metal dusting occurs at very high penetration rates. Penetration rates as high as 1000 mpy have been reported. It results from the following two reactions when the carbon activity is above 1.

Water Gas Shift Reaction:

$$CO+H_2O \leftrightarrow CO_2+H_2$$

Boudouard Reaction:

$$2CO \leftrightarrow CO_2+C$$

b) The very high penetration rates caused by metal dusting are observed in wrought alloys where grains of metal are extracted from the surface as the grain boundaries are rapidly penetrated. In cast alloys, these same conditions result in a form of damage commonly termed “green rot.” In cast alloys, the interdendritic regions are rapidly penetrated leaving an oxide scale; however, the individual dendrites are not extracted from the surface because they are held in place due to the jagged nature of the interdendritic region.

3.44.2 Affected Materials

Low-alloy steels, 300 series SS, nickel-based alloys, and heat-resisting alloys. There is currently no known metal alloy that is immune to metal dusting under all conditions. Aluminized coatings that form a protective alumina layer on the surface have been shown to provide some protection against metal dusting.

3.44.3 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 that is normally found in syn gas generation processes and steam reforming heaters when conditions become reducing and the carbon activity is above 1.

d) It usually occurs in the approximate operating temperature range of 900 °F to 1500 °F (480 °C to 815 °C). Damage increases with increasing temperature up to about 1500 °F (815 °C). Above about 1500 °F (815 °C), the calculated carbon activity for the water gas shift reaction and the Boudouard reaction will decrease to levels below 1, where metal dusting cannot occur. On the lower end of the temperature range for metal dusting, the calculated carbon activity will still be high and above 1; however, the reaction kinetics will be slow, and the metal loss will be limited.

e) The mechanism of metal dusting is considered to involve:

1. saturation of the metal matrix by carburization;
2. precipitation of metal carbides at the metal surface and grain boundaries;
3. deposition of graphite from the atmosphere onto the metal carbides at the surface;
4. decomposition of the metal carbides under the graphite and metal particles; and
5. 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 preferentially attacks the grain boundaries, resulting in the removal of metal grains that form what appears to be a “metal dust.”

3.44.4 Affected Units or Equipment

a) Metal dusting occurs in processes that contain a gas composition that includes the gases shown in the water gas shift and Boudouard reactions above.

b) Metal dusting has been reported in gas turbines, methanol reforming unit outlet piping, thermal hydrodealkylation furnaces and reactors, outlets of steam reformer heaters, and POX units.

3.44.5 Appearance or Morphology of Damage

a) In low-alloy steels, the wastage is typically severe, and can be uniform, but usually is in the form of small pits filled with a crumbly residue of metal particles and carbon soot. There may be areas of numerous rounded pits, uniform thinning, and/or thru-wall perforations.

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 3-44-1)

d) Metallography will show that the metal is carburized under the attacked surface. (Figure 3-44-2)

3.44.6 Prevention/Mitigation

a) Sulfur in the carburizing atmosphere (usually as H_2S or a disulfide) forms a protective sulfur atmosphere on the surface that preferentially prevents carbon from being absorbed onto the surface. For protection, a low level of a reactive sulfur species such as H_2S or a disulfide must always be in the process environment. Typically, sulfur levels less than 10 ppm are needed to mitigate metal dusting. Higher sulfur levels should not be injected since it can promote sulfidation and adversely affect the activity of catalyst, if present.

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) In many cases, equipment is refractory lined to keep metal temperatures below the range where metal dusting occurs.

d) An aluminum diffusion treatment (such as alonizing) applied to the base metal can be beneficial in some applications.

e) Control of the process stream composition to ensure the carbon activity is maintained below 1 can effectively prevent metal dusting. In a steam reformer heater that is forming a syn gas, metal dusting can be prevented by maintaining the steam-to-carbon ratio of the feed above 2 to 3.

3.44.7 Inspection and Monitoring

Metal dusting normally occurs so rapidly that it is noticed only after a failure has occurred and metal loss has occurred through the wall.

a) Metal dusting is most accurately confirmed through destructive testing, i.e. sampling for chemical or physical evidence.

b) If internal surfaces are accessible, VT can be effective in identifying areas of severe metal wastage, including localized areas of numerous rounded pits, uniform thinning, and thru-wall perforations.

c) RT techniques can be employed to look for pitting, cracking, and wall thinning.

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

e) A specialized methodology combining intelligent pigging technology with an advanced engineering assessment has shown success in detecting and quantifying the damage mechanism.

3.44.8 Related Mechanisms

Carburization (3.13).

3.44.9 References

1. API Recommended Practice 573, *Inspection of Fired Boilers and Heaters*, American Petroleum Institute, Washington, DC.

2. H.J. Grabke, "Metal Dusting of Low- and High-alloy Steels," *CORROSION*, Vol. 51, 1995, p. 711.

3. H.J. Grabke, R. Krajak, and J.C. Nava Paz, "On the Mechanism of Catastrophic Carburization: Metal Dusting," *Corrosion Science*, Vol. 35, Nos. 5–8, 1993, p. 1141.

4. B.A. Baker and G.D. Smith, "Metal Dusting of Nickel-Containing Alloys," Paper No. 445, *Corrosion/98*, NACE International, Houston, TX.

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6. *Corrosion Control in the Petrochemical Industry*, ASM International, ISBN-13: 9780871705051, 1994, pp. 231–233.

7. D.H. Herring, "What to Do About Metal Dusting," *Heat Treat Progress*, 2003, pp. 20–24.

8. P.J. Van De Loo, A. Wolfert, R. Schelling, H.J. Schoorlemmer, and T.M. Kooistra, "Low-alloy Steel Metal Dusting: Detailed Analysis by Means of Acoustic Emission," *Journal of Acoustic Emission*, Vol. 20, 2002, pp. 238–247.

Figure 3-44-1—Metal dusting of a 304H stainless steel pipe.

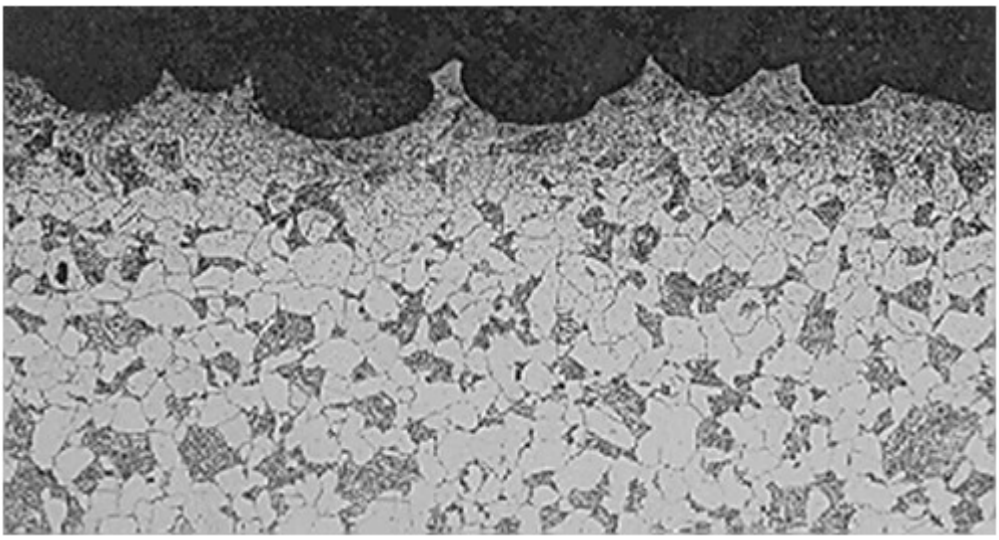

Figure 3-44-2—Carbon steel separator plate in a natural gas preheater showing classical pattern of carburization and pitting.

3.45 Microbiologically Influenced Corrosion

3.45.1 Description of Damage

Corrosion caused by living organisms such as bacteria, algae, or fungi. It is often associated with the presence of tubercles or slimy organic substances. Often, the bacteria produce localized corrosion in the form of pitting or crevice corrosion.

3.45.2 Affected Materials

Most common materials of construction including carbon and alloy steels, 300 series SS and 400 series SS, aluminum alloys, copper alloys, and some nickel alloys. Titanium appears to be highly resistant.

3.45.3 Critical Factors

a) Microbiologically influenced corrosion (MIC) is found in aqueous environments. Occasionally it is found in services where water is intermittently present. Stagnant or low-flow conditions allow and/or promote the growth of microorganisms.

b) Because there are many types, organisms can survive and grow under a wide range of conditions including lack of oxygen, light or dark, high salinity, pH range of 0 to 12, and temperatures from 0 °F to 235 °F (–15 °C to 115 °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, iron, sulfate compounds, and H_2S) and organic substances (e.g. hydrocarbons and organic acids). In addition, all organisms require a source of carbon, nitrogen, and phosphorous for growth. Corrosion is often blamed on iron-oxidizing bacteria or SRB. However, these organisms are typically only part of a complex colony of multiple types of interdependent organisms, each capable of creating by-products that might be a food source for others.

e) In-leakage of process contaminants such as hydrocarbons or H_2S may lead to a massive increase in biofouling and corrosion.

3.45.4 Affected Units or Equipment

a) MIC is often found in water-cooled heat exchangers, in the bottom water layer of storage tanks, in piping with stagnant or low flow, and in piping in contact with some soils.

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

   2. Stagnant process lines with trapped water can suffer from MIC.

b) Drain systems and other water-containing systems associated with docks and ship loading/unloading facilities can experience MIC.

c) MIC is commonly found in equipment where the hydrotest water has not been removed or where equipment has been left outside and unprotected. 300 series SS are often affected unless precautionary measures are taken.

d) Fire-water systems can be affected.

3.45.5 Appearance or Morphology of Damage

a) MIC corrosion is frequently observed as localized pitting under deposits or tubercles that shield the organisms. Tubercles also form on carbon steel exposed to oxygenated water, so the presence of tubercles is not a guarantee of MIC.

b) Damage is often characterized by cup-shaped pits within pits (the halo effect) in carbon steel or subsurface cavities in stainless steel. (Figure 3-45-1 to Figure 3-45-7) However, these pits are often indistinguishable from under-deposit corrosion in carbon steel and chloride pitting in stainless steels. Pit morphology alone may not be a reliable indicator of the cause of corrosion.

3.45.6 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. Often, multiple biocides are needed to keep the levels of bacteria in the appropriate ranges.

b) Proper application of biocides will control, but not eliminate, microbes; therefore, continued treatment is often necessary.

c) Periodically flushing and cleaning susceptible systems will help minimize colony growth and resultant MIC.

d) Minimize low-flow or stagnant zones in water-containing systems. A flow rate of 3 fps (1 m/s) will inhibit colony formation and thereby minimize the likelihood of MIC.

e) Lines should be sloped to assist in drainage.

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

g) Empty hydrotest water as soon as possible. Remove moisture and prevent additional moisture intrusion.

h) Coating and cathodically protecting underground structures and interiors of storage tanks have been shown to be effective mitigation methods for MIC.

i) Biocides are generally not effective in a system that is already contaminated with colonies protected by a sludge layer. Effective mitigation of established organisms requires complete removal of deposits and organisms, typically using some combination of pigging, blasting, chemical cleaning, and biocide treatment.

3.45.7 Inspection and Monitoring

a) In cooling water systems, effectiveness of treatment is monitored by measuring biocide residual, microbe counts, and visual appearance of the water. Sampling and analysis can be performed to better understand the bacteria population (e.g. ATP, qPCR). While effective treatment and monitoring are key to identifying the potential for MIC, it still can occur in areas with stagnant flow. Also, the type of microorganisms being investigated should be identified to ensure proper incubation of water samples (e.g. using an appropriate temperature for incubation for thermophilic bacteria).

b) Special probes have been designed to monitor for evidence of fouling that may precede or coincide with MIC damage. Corrosion coupons can be used to identify MIC by sampling the coupon surface after it is pulled from service; however, it should be noted that just because sessile bacteria populations are not found on the coupon, it does not mean they do not exist in the system.

c) An increase in the loss of duty of a heat exchanger may be indicative of fouling and potential MIC damage. RFT can be performed to gauge depth of corrosion on heat exchanger tubes.

d) Foul smelling water may indicate biological activity.

e) MIC is often highly localized, so a technique that can find localized corrosion should be chosen, as applicable to the circumstances (e.g. VT, AUT, or RT).

3.45.8 Related Mechanisms

Cooling water corrosion (3.20), brine corrosion (3.10), oxygenated water corrosion (3.49), and concentration cell corrosion (3.19).

3.45.9 References

1. D.H. Pope and J.G. Stoecker, "Microbiologically Influenced Corrosion," *Process Industries Corrosion—The Theory and Practice*," NACE International, Houston, TX, 1986, pp. 227–242.

2. T.J. Tvedt, Jr., "Cooling Water Systems," *Corrosion Control in the Refining Industry*, NACE Course Book, NACE International, Houston, TX, 1999.

3. S.C. Dexter, "Biologically Induced Corrosion," *NACE Proceedings of the International Conference on Biologically Induced Corrosion, June 10–12, 1985*, NACE International, Houston, TX.

4. B.J. Little and J.S. Lee, *Microbiologically Influenced Corrosion*, John Wiley & Sons, 2007.

5. NACE TM0194, *Field Monitoring of Bacterial Growth in Oil and Gas Systems*, NACE International, Houston, TX.

Figure 3-45-1—MIC on a diesel tank bottom.

Figure 3-45-2—Pitting corrosion on the ID of a 6-in. carbon steel sour crude line after 2½ years of service. Pits are approximately 1-in. to 2-in. wide. Note the halo effect in Figure 3-43-3.

Figure 3-45-3—Same pipe as Figure 3-43-2. Note the halo effect.

Figure 3-45-4—Oil line with MIC damage beneath tubercles.

Figure 3-45-5—Same oil line as Figure 3-43-4. Hemispherical pitting typical of MIC can be seen after grit blasting to remove the scale.

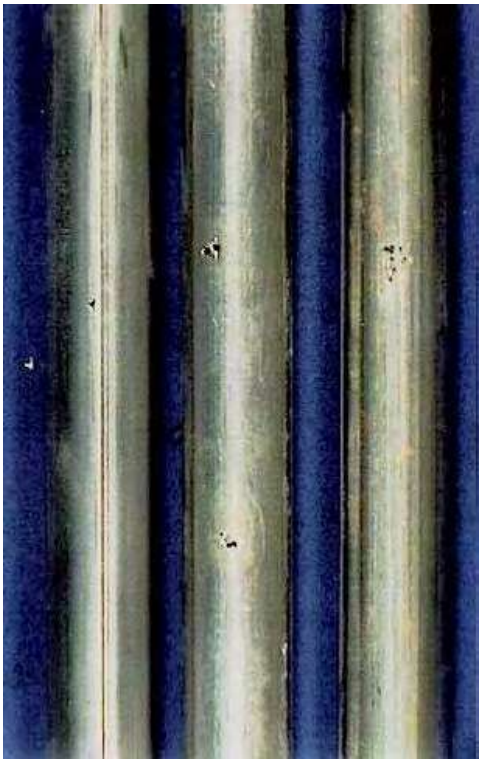

Figure 3-45-6—Type 304 stainless steel exchanger tubes failed from pitting corrosion on the shell side in cooling water service after 2½ years without biocide treatment.

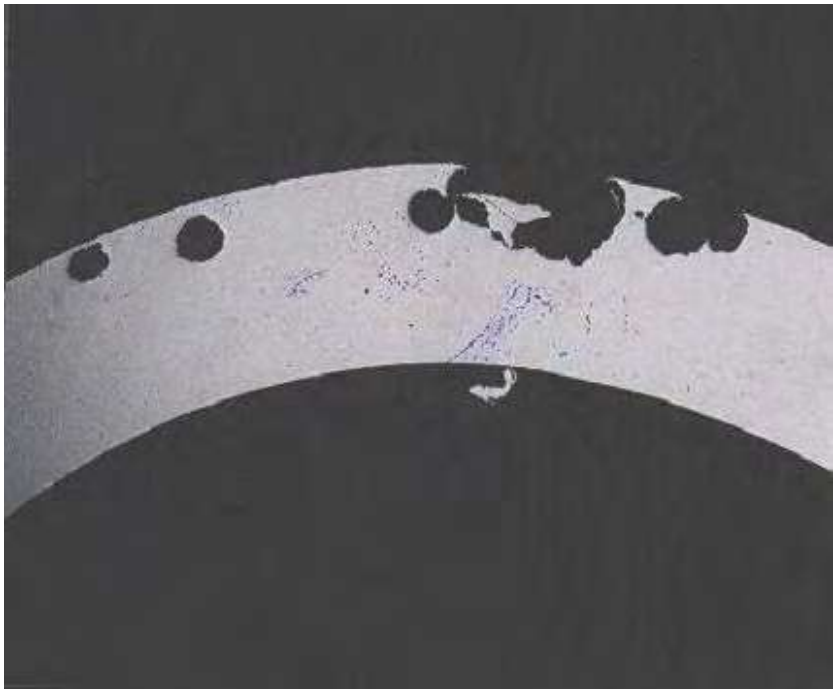

Figure 3-45-7—A cross section of the tube in Figure 3-43-6 revealing severe subsurface tunneling, typical of MIC.

3.46 Naphthenic Acid Corrosion

3.46.1 Description of Damage

A form of high-temperature corrosion that occurs primarily in crude and vacuum units caused by organic naphthenic acids in the crude oil, as well as downstream units that process certain fractions or cuts that contain naphthenic acids.

3.46.2 Affected Materials

Carbon steel, low-alloy steels, 400 series SS, 300 series SS, and nickel-based alloys. See Table 3-46-1.

3.46.3 Critical Factors

a) Naphthenic acid corrosion (NAC) is a function of the naphthenic acid content, temperature, sulfur content, velocity (wall shear stress), and alloy composition.

b) Severity of corrosion increases with increasing acidity of the hydrocarbon phase.

c) Neutralization number or TAN is a measure of the acidity (organic acid content) as determined by various test methods such as ASTM D664. However, NAC occurs in hot dry hydrocarbon streams that do not contain a free water phase.

d) The TAN of the crude may be misleading, because the correlation between whole crude TAN and corrosion rate is poor, especially when comparing different crudes. A high TAN crude may be less corrosive than a moderate or low TAN crude. This is because this family of organic acids that together are referred to as naphthenic acid, has a range of boiling points and tends to concentrate in various cuts. Therefore, the occurrence and severity of NAC are determined by the naphthenic acids present in the actual stream, not the crude charge. Additional factors are the following.

    1. TAN is a measure of the total amount of all acids in the crude, not just naphthenic acids.

    2. The various acids that comprise the naphthenic acid family can have distinctly different corrosivity.

    3. The structure and molecular weight of the specific naphthenic acids present have a strong impact on corrosivity, but they are not determined by TAN measurements.

e) No widely accepted prediction methods have been developed to correlate corrosion rate with the various factors influencing it.

f) Sulfur promotes iron sulfide formation and has an inhibiting effect on NAC, up to a point.

g) Naphthenic acids remove protective iron sulfide scales on the surface of metals.

h) NAC can be a particular problem with very low sulfur crudes. While a crude TAN threshold of 0.30 is typically cited as the TAN level below which NAC is not expected, some NAC cases have been reported with low sulfur and crude TAN as low as 0.10.

i) NAC primarily occurs in hot streams above 425 °F (220 °C) but has been reported as low as 350 °F (175 °C). Severity increases with temperature up to about 750 °F (400 °C); however, NAC has been observed in hot coker gas oil streams up to 800 °F (425 °C).

j) Naphthenic acids are destroyed by catalytic reactions in downstream hydroprocessing and FCC units. NAC of 300 series SS is also inhibited by injection of hydrogen in the feed to hydroprocessing units.

k) Alloys containing increasing amounts of molybdenum show improved resistance to NAC. While alloys with a minimum of 2 % Mo, e.g. Types 316 and 316L SS, have demonstrated adequate resistance in some applications, it is generally agreed based on industry experience that alloys with a minimum of 3 % Mo, e.g.

Types 317 and 317L SS, are needed avoid NAC. To provide a greater degree of assurance, alloys with a minimum of 4 % Mo, e.g. Type 317LM, are sometimes selected. Under severe conditions or for components with nil corrosion allowance, 6 % Mo stainless steels and Alloy 625 have been used.

l) Corrosion is most severe in two-phase (liquid and vapor) flow, in areas of high velocity or turbulence, and in distillation towers where hot vapors condense to form liquid phase droplets.

1. For piping, NAC typically occurs in high-velocity and turbulent areas. The vapor space may be more susceptible to corrosion when flow is two phase due to acid condensation.

3.46.4 Affected Units or Equipment

a) Crude and vacuum heater tubes, crude and vacuum heater transfer lines, vacuum bottoms piping, atmospheric gas oil (AGO) circuits, and heavy vacuum gas oil (HVGO) and sometimes light vacuum gas oil (LVGO) circuits. NAC has also been found in resid transfer lines from the vacuum unit to the coker. Although thermal cracking in the delayed coker is thought to break down naphthenic acids, making NAC uncommon in coker units, NAC has been reported in the light coker gas oil (LCGO) and heavy coker gas oil (HCGO) streams in delayed coking units processing high TAN feed.

b) Piping systems are particularly susceptible in areas of high velocity, turbulence, or change of flow direction. Examples include pump internals, valves, elbows, tees, and reducers as well as areas of flow disturbance such as weld beads and thermowells.

c) Crude and vacuum tower internals may also be corroded in the flash zones and packing and internals may corrode where high-acid streams condense or high-velocity droplets impinge.

d) NAC may be found in hot hydrocarbon streams in units downstream of the crude and vacuum units, upstream of any hydrogen mix points.

3.46.5 Appearance or Morphology of Damage

a) NAC is characterized by localized corrosion, pitting corrosion, or flow-induced grooving in high-velocity areas. (Figure 3-46-1 and Figure 3-46-2)

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

c) At temperatures below ~450 °F (230 °C), NAC can have a smoother, more uniform appearance than is typical at higher temperatures.

3.46.6 Prevention/Mitigation

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

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

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

c) Use alloys with higher molybdenum content for improved resistance. Type 317L SS or other alloys with higher molybdenum content may be required.

d) High-temperature NAC inhibitors have been used with moderate success in reducing corrosion rates. However, their potential detrimental effects on downstream catalyst activity must be considered. Phosphorus-based inhibitors tend to be more effective but have more detrimental effect on downstream catalyst than sulfur-based inhibitors. Inhibitors effectiveness needs to be monitored carefully.

3.46.7 Inspection and Monitoring

Localized wall loss due to NAC is difficult to predict and find.

a) VT can be used where access is available.

b) RT can be used to look for and identify the extent of localized wall loss.

c) Close-grid UT thickness examination or UT thickness scanning can also be used, either as an alternative to RT, e.g. when RT is not practical due to piping size or configuration, or as a follow-up to RT.

d) Permanently mounted thickness monitoring sensors can be used.

e) Electrical resistance corrosion probes, hydrogen probes, and corrosion coupon racks can be used if properly located. However, caution needs to be exercised with intrusive devices such as ER probes and coupons since they may create the turbulence that results in corrosion not only of the measuring device but of the adjacent pipe wall.

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

3.46.8 Related Mechanisms

Sulfidation (3.61) is a competing and complimentary mechanism that must be considered in most situations with NAC. In cases where thinning is occurring, it may be difficult to distinguish between NAC and sulfidation, and both may be contributing to wall loss, but pitting damage is attributable to NAC.

3.46.9 References

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2. J. Gutzeit, “Naphthenic Acid Corrosion,” Paper No. 156, *Corrosion/76*, NACE International, Houston, TX.

3. R.L. Piehl, “Naphthenic Acid Corrosion in Crude Distillation Units,” *Materials Performance*, January 1988.

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6. API Recommended Practice 581, *Risk-Based Inspection Methodology,* American Petroleum Institute, Washington, DC.

7. C. Shargay et al., “Survey of Materials in Hydrotreater Units Processing High Tan Feeds,” Paper No. 07573, *Corrosion/2007*, NACE International, Houston, TX.

Table 3-46-1—Alloys Listed in Approximate Order of Increasing Resistance to NAC

CS, 1¼Cr-½Mo, 2¼Cr-1Mo,
5Cr-½Mo
9Cr-1Mo, 410 SS, 304L SS, 321 SS, 347 SS
316 SS (2 % to 3 % Mo)
317 SS (3 % to 4 % Mo)
6 % Mo alloys
Alloy 625, Alloy 276
NOTE Alloys listed above 316 SS in the table are not considered NAC-resistant materials.

Figure 3-46-1—Erosion-corrosion damage due to NAC in a 10-in. 5Cr-½Mo elbow in the outlet of a vacuum heater in a vacuum distillation unit.

Figure 3-46-2—Severe NAC of 410 SS trays and bubble caps in the HVGO section of the vacuum tower fed by the vacuum heater referred to in Figure 3-44-1.

3.47 Nitriding

3.47.1 Description of Damage

Nitriding is the formation of a hard, brittle surface layer on some alloys due to exposure to high-temperature process streams containing high levels of nitrogen compounds such ammonia or cyanides, particularly under reducing conditions. It may adversely affect corrosion resistance, creep strength, ductility and fracture toughness, and weldability.

In most cases, a harder surface layer of a vessel or component by itself will not affect its mechanical integrity. However, the concern is for cracks developing in the nitrided layer and propagating into the base metal.

Nitriding of the surface is also done as a manufacturing process to surface harden (case harden) components to provide improved abrasion and wear resistance.

3.47.2 Affected Materials

a) Carbon steel, low-alloy steels, 400 series SS, and 300 series SS are affected.

b) Nickel-based alloys are more resistant.

3.47.3 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/dissociation of nitrogen from ammonia or other compounds and for diffusion of nitrogen into the metal. Since diffusion is a function of time, longer exposure times at elevated temperature increase the amount and depth of nitriding.

c) Nitriding begins above 600 °F (315 °C) and becomes more rapid and severe above 900 °F (480 °C).

d) Above 770 °F (410 °C), preferential grain boundary nitriding may lead to microcracking and embrittlement.

e) High gas phase nitrogen activity (i.e. high partial pressure of nitrogen) promotes nitriding.

f) Alloys containing 30 % to 80 % nickel are more resistant.

3.47.4 Affected Units or Equipment

Nitriding can occur wherever appropriate environment and temperature conditions exist, but it is fairly uncommon in refining. Nitriding has been observed in steam-methane reformers, steam-gas cracking (olefin) plants, and ammonia synthesis plants.

3.47.5 Appearance or Morphology of Damage

a) An example of surface cracking resulting from nitriding is shown in Figure 3-47-1 to Figure 3-47-3.

b) Nitriding is usually confined to the surface of most components and will have a dull, dark gray appearance. (Figure 3-47-1) However, confirmation normally requires metallography as shown in Figure 3-47-2 and Figure 3-47-3, which delineate the nitrided layer as well as showing the cracks within that layer.

1. When nitrogen diffuses into the surface, it forms needle-like particles of iron nitrides (Fe_3N or Fe_4N) that can only be confirmed by metallography.

c) In a more advanced stage, the material will exhibit very high surface hardness, which may be identifiable by surface hardness measurement but is readily measured by microhardness testing of metallographic samples. (Figure 3-47-3)

d) Nitriding of low-alloy steels containing up to 12 % chromium is accompanied by an increase in volume, and the nitrided layer tends to crack and flake.

e) 300 series SS tend to form thin, brittle layers that may crack and spall from thermal cycling or applied stress.

3.47.6 Prevention/Mitigation

Where nitriding is an issue serious enough to require a remedy, changing to a more resistant alloy with 30 % to 80 % nickel is usually necessary. It is normally not practical to modify the process conditions to reduce the nitrogen partial pressure or lower the temperature.

3.47.7 Inspection and Monitoring

Various surface inspection techniques can be used detect nitriding, particularly in the advanced stages. Destructive testing is generally required to confirm the damage mechanism and the depth of penetration.

a) Materials exposed to nitriding conditions should be inspected thoroughly because good appearance may mask damage. A change in surface color to a dull gray may indicate nitriding.

    1. Cast furnace tubes exposed to nitriding flue gas may change from a rough as-cast appearance to a smooth glazed appearance due to spalling of the nitride layer.

b) Nitriding will generally affect the entire exposed surface. Where process conditions are the same, focus inspection on areas where the external temperature would most favor nitriding.

c) Hardness testing of the affected surfaces can help indicate nitriding, because hardness of 400 to 500 HB or higher can result. However, depending somewhat on the hardness test device used, surface hardness testing results will be a mix of the hard surface layer and the softer material beneath it and therefore may not be definitive.

d) Nitrided layers are magnetic. 300 series SS should be checked for magnetism as an initial screening. However, some cast 300 series SS alloys are magnetic and could yield a false positive.

e) Metallography is generally required to confirm nitriding and to determine the depth of penetration of the nitride layer.

f) ECT may be used in some cases to detect nitriding, including prior to any crack formation.

g) In the advanced stages of nitriding, where surface cracking may have initiated, appropriate inspection techniques include PT, MT, and angle beam UT (SWUT or PAUT).

3.47.8 Related Mechanisms

Similar mechanisms involving gas diffusion into the surface layer of the metal include carburization (3.13) and metal dusting (3.44).

3.47.9 References

1. *ASM Handbook—Corrosion,* Volume 13, ASM International, Materials Park, OH.

2. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, pp. 93–94.

3. J. Scherzer and D.P. McArthur, “Test Shows Effects of Nitrogen Compounds on Commercial Fluid Cat Cracking Catalysts,” *Oil and Gas Journal*, Vol. 84, 1986, pp. 76–82.

Figure 3-47-1—A nitrided 5Cr-½Mo thermowell tube from an ammonia synthesis plant with surface cracking.

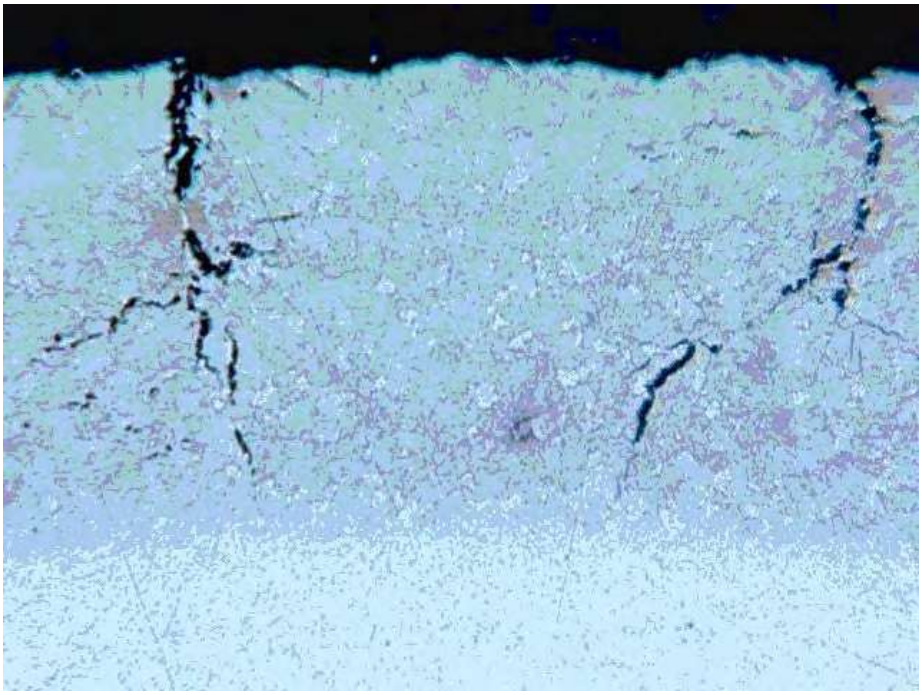

Figure 3-47-2—A photomicrograph of a cross section though the tube in Figure 3-45-1 showing the interface between the shallow nitrided layer on the surface (gray) and the unaffected base metal (white). Cracks initiated from the OD surface at the top. Magnification 50X.

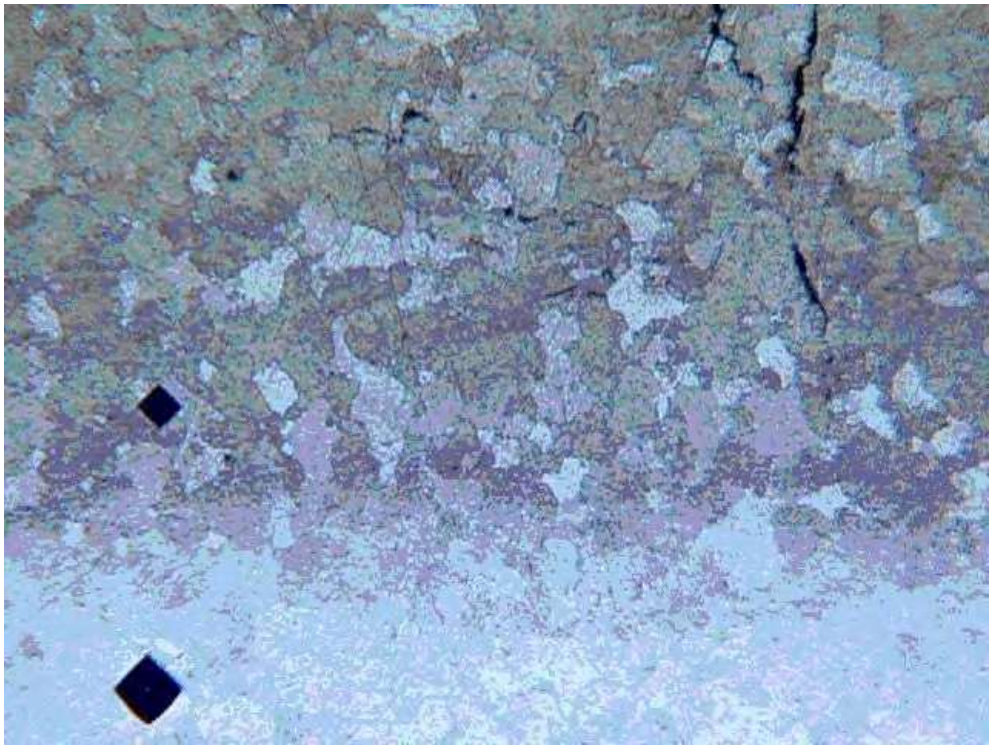

Figure 3-47-3—A higher-magnification photomicrograph of the same tube showing the smaller diamond-shaped hardness indentation in the hard nitrided layer (540 HB) vs the larger indentation in the softer base metal (210 HB). Magnification 150X.

3.48 Oxidation

3.48.1 Description of Damage

Oxygen, most often present as a component of air (approximately 21 %), reacts with carbon steel and other alloys at high temperature, converting the metal to oxide scale and thereby reducing the metal wall thickness.

3.48.2 Affected Materials

a) All iron-based materials including carbon steel and low-alloy steels, both cast and wrought, are affected.

b) All 300 series SS, 400 series SS, and nickel-based alloys also oxidize to varying degrees, depending on composition and temperature.

3.48.3 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 (540 °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 (815 °C). See Table 3-48-1a and Table 3-48-1b and Figure 3-48-1.

d) The presence of water vapor can significantly accelerate oxidation rates of some steels including 9Cr-1Mo. (Reference 4)

3.48.4 Affected Units or Equipment

Significant oxidation occurs in fired heaters, boilers, and other combustion equipment, as well as piping and equipment that operate in high-temperature, oxygen-containing environments where metal temperatures exceed about 1000 °F (540 °C).

3.48.5 Appearance or Morphology of Damage

a) Carbon steel, low-alloy steels, and 12Cr stainless 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 3-48-2 to Figure 3-48-4).

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.

3.48.6 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 effects on mechanical properties. They are often used in special alloys for applications such as heater supports, burner tips, and components for combustion equipment.

3.48.7 Inspection and Monitoring

a) Process conditions should be monitored to establish trends of high-temperature equipment where oxidation can occur.

b) Temperatures can be monitored with tube-skin thermocouples and/or infrared thermography.

c) RT can be used to measure remaining thickness when oxidation occurs on the external surface. Alternatively, the oxide could be removed, e.g. using a flapper wheel, to allow UT measurement of the remaining wall thickness.

d) UT can be used to measure remaining thickness when oxidation occurs on the internal surface.

e) EMAT has been used to measure general external wall loss on heater tubes.

3.48.8 Related Mechanisms

Other high-temperature gas corrosion mechanisms are sulfidation (3.61), high-temperature H_2/H_2S corrosion (3.35), carburization (3.13), and metal dusting (3.44). 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.

3.48.9 References

1. API Recommended Practice 581, *Risk-Based Inspection Technology*, American Petroleum Institute, Washington, DC, Second Edition, 2008.

2. J. Gutzeit, R.D. Merrick, and L.R. Scharfstein, "Corrosion in Petroleum Refining and Petrochemical Operations," *Metals Handbook*, Volume 13, ASM International, Materials Park, OH, 1987, pp. 1262–1287.

3. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, pp. 276–288.

4. F. Dettenwanger et al., "The Influence of Si, W and Water Vapor on the Oxidation Behavior of 9Cr Steels," Paper No. 01151, *Corrosion/2001*, NACE International, Houston, TX.

Table 3-48-1a—Estimated Oxidation Rates (mpy) (Reference 1)

Material	Maximum Metal Temperature (°F)											
	925	975	1025	1075	1125	1175	1225	1275	1325	1375	1425	1475
CS	2	4	6	9	14	22	33	48	—	—	—	—
1¼Cr	2	3	4	7	12	18	30	46	—	—	—	—
2¼Cr	1	1	2	4	9	14	24	41	—	—	—	—
5Cr	1	1	1	2	4	6	15	35	65	—	—	—
7Cr	1	1	1	1	1	2	3	6	17	37	60	—
9Cr	1	1	1	1	1	1	1	2	5	11	23	40
12Cr	1	1	1	1	1	1	1	1	3	8	15	30
304 SS	1	1	1	1	1	1	1	1	1	2	3	4
309 SS	1	1	1	1	1	1	1	1	1	1	2	3
310 SS/HK	1	1	1	1	1	1	1	1	1	1	1	2
800 H/HP	1	1	1	1	1	1	1	1	1	1	1	2
Material	**Maximum Metal Temperature (°F)**											
	1525	**1575**	**1625**	**1675**	**1725**	**1775**	**1825**	**1875**	**1925**	**1975**	**2025**	**2075**
CS	—	—	—	—	—	—	—	—	—	—	—	—
1¼Cr	—	—	—	—	—	—	—	—	—	—	—	—
2¼Cr	—	—	—	—	—	—	—	—	—	—	—	—
5Cr	—	—	—	—	—	—	—	—	—	—	—	—
7Cr	—	—	—	—	—	—	—	—	—	—	—	—
9Cr	60	—	—	—	—	—	—	—	—	—	—	—
12Cr	50	—	—	—	—	—	—	—	—	—	—	—
304 SS	6	9	13	18	25	35	48	—	—	—	—	—
309 SS	4	6	8	10	13	16	20	30	40	50	—	—
310 SS/HK	3	4	5	7	8	10	13	15	19	23	27	31
800 H/HP	3	4	6	8	10	13	17	21	27	33	41	50

Table 3-48-1b—Estimated Oxidation Rates (mm/yr) (Reference 1, converted)

Material	Maximum Metal Temperature (°C)											
	495	525	550	580	605	635	665	690	720	745	775	800
CS	0.05	0.1	0.15	0.23	0.36	0.56	0.84	1.22	—	—	—	—
1¼Cr	0.05	0.08	0.1	0.18	0.3	0.46	0.76	1.17	—	—	—	—
2¼Cr	0.03	0.03	0.05	0.1	0.23	0.36	0.61	1.04	—	—	—	—
5Cr	0.03	0.03	0.03	0.05	0.1	0.15	0.38	0.89	1.65	—	—	—
7Cr	0.03	0.03	0.03	0.03	0.03	0.05	0.08	0.15	0.43	0.94	1.52	—
9Cr	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.13	0.28	0.58	1.02
12Cr	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.08	0.2	0.38	0.76
304 SS	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.08	0.1
309 SS	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.08
310 SS/HK	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05
800 H/HP	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05
Material	**Maximum Metal Temperature (°C)**											
	830	855	885	915	940	970	995	1025	1050	1080	1105	1135
CS	—	—	—	—	—	—	—	—	—	—	—	—
1¼Cr	—	—	—	—	—	—	—	—	—	—	—	—
2¼Cr	—	—	—	—	—	—	—	—	—	—	—	—
5Cr	—	—	—	—	—	—	—	—	—	—	—	—
7Cr	—	—	—	—	—	—	—	—	—	—	—	—
9Cr	1.52	—	—	—	—	—	—	—	—	—	—	—
12Cr	1.27	—	—	—	—	—	—	—	—	—	—	—
304 SS	0.15	0.23	0.33	0.46	0.64	0.89	1.22	—	—	—	—	—
309 SS	0.10	0.15	0.20	0.25	0.33	0.41	0.51	0.76	1.02	1.27	—	—
310 SS/HK	0.08	0.10	0.13	0.18	0.20	0.25	0.33	0.38	0.48	0.58	0.69	0.79
800 H/HP	0.08	0.10	0.15	0.20	0.25	0.33	0.43	0.53	0.69	0.84	1.04	1.27

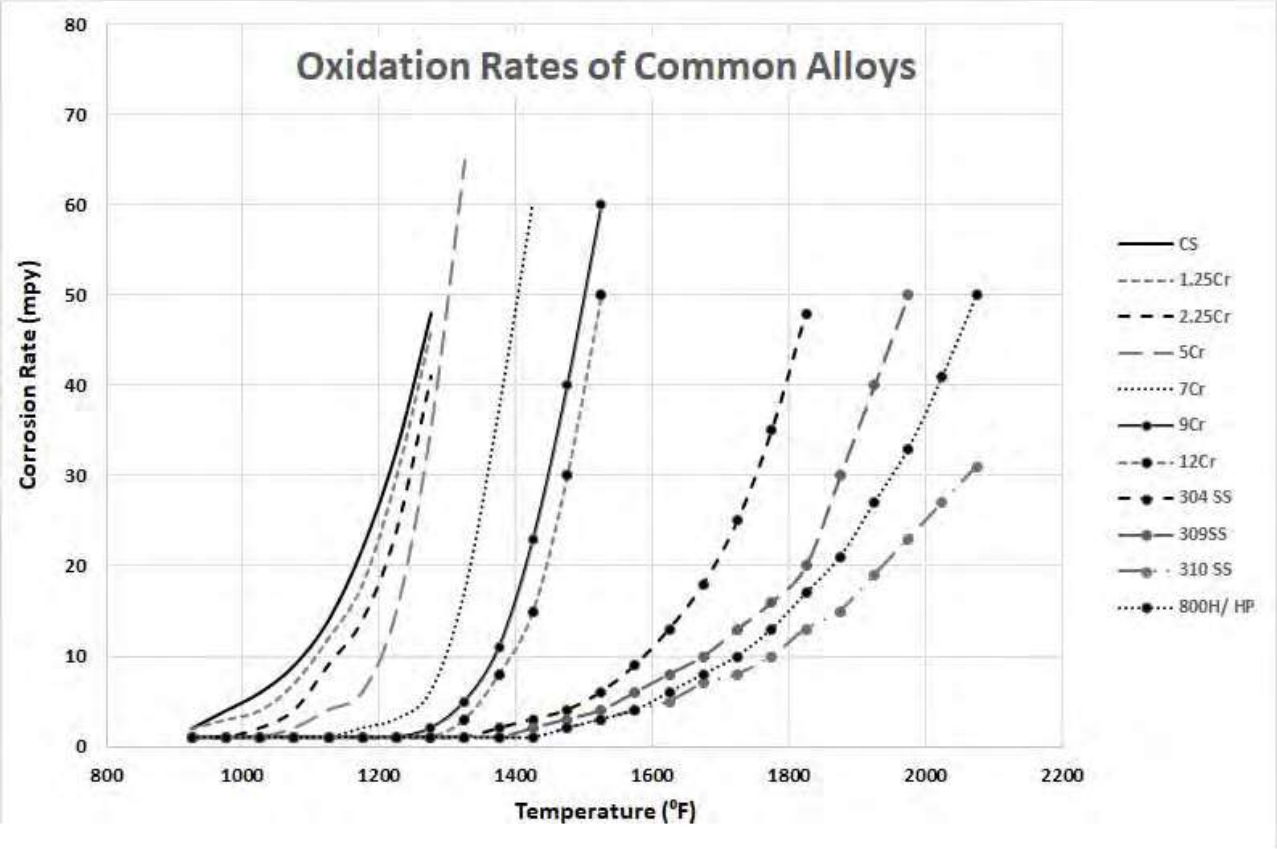

Figure 3-48-1—Estimated oxidation rates based on the data in Table 3-46-1a.

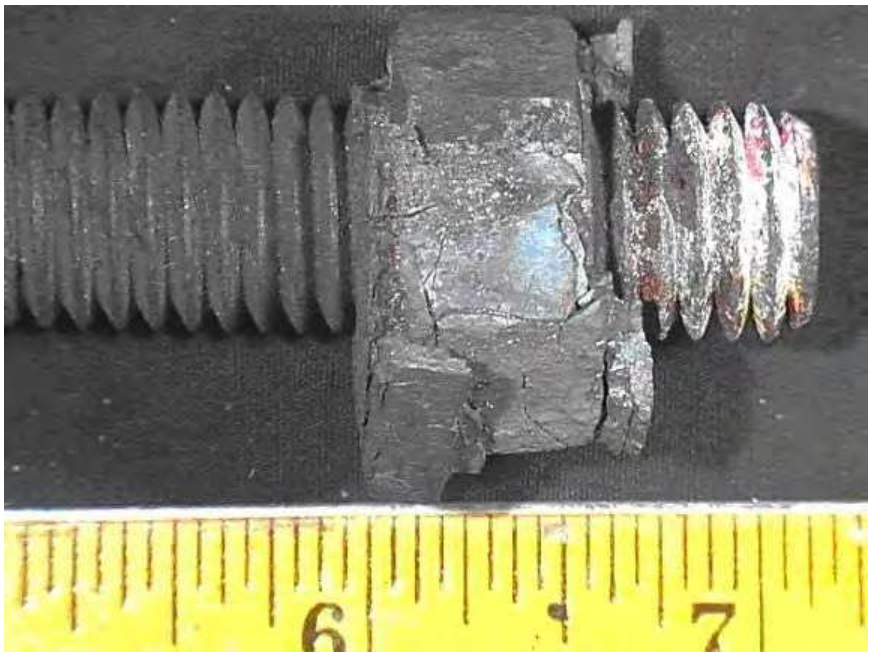

Figure 3-48-2—Oxidation of a carbon steel nut on a stainless steel stud at 1300 °F (705 °C).

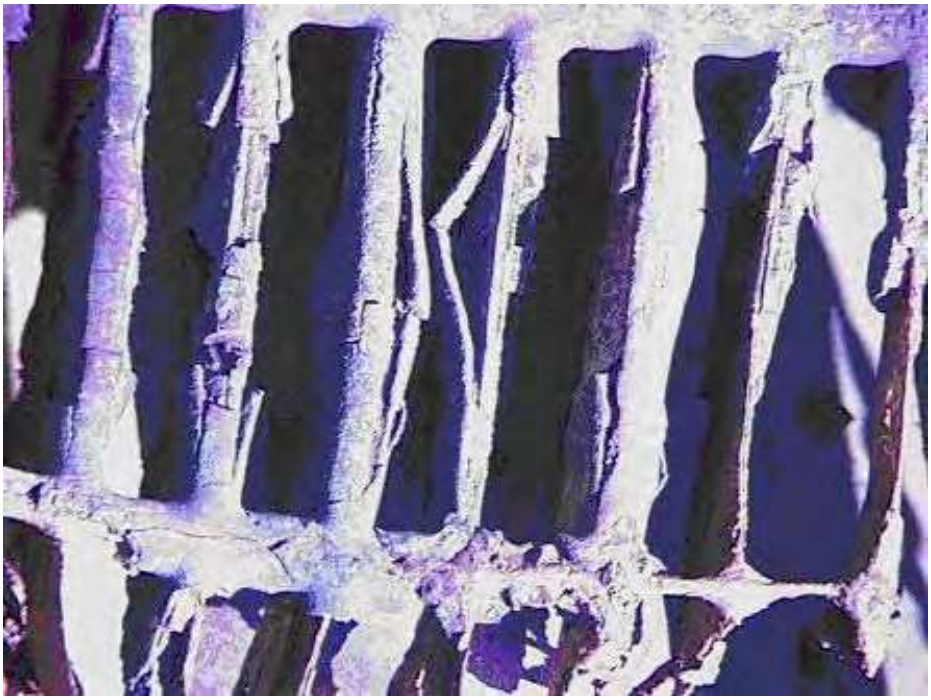

Figure 3-48-3—Oxidation of a carbon steel grid from a sulfur reactor.

Figure 3-48-4—Oxidation of the OD of a carbon steel furnace transfer line.

3.49 Oxygenated Process Water Corrosion

3.49.1 Description of Damage

The presence of oxygen-containing water in refining process streams can significantly increase corrosion activity. Because the solubility of oxygen increases as the temperature of the water decreases, the corrosion activity due to oxygen-containing water tends to be higher at lower temperatures.

3.49.2 Affected Materials

Carbon steel and low-alloy steels.

3.49.3 Critical Factors

a) Water has to be present as a liquid phase, so the process temperature and pressure must allow for liquid water to be present. Given the presence of water, the critical factors are oxygen solubility and content, temperature, and velocity and turbulence.

b) Oxygen solubility and content.

1. Only trace levels (about 20 ppb) of oxygen are needed to significantly increase corrosion rates, and if the O_2 partial pressure in the vapor phase increases (e.g. due to more air getting into the vapor phase and thereby increasing the concentration of oxygen in the vapor phase), so does the concentration of oxygen in the water phase. As long as there is a vapor phase in the system, a higher system pressure will force more oxygen to dissolve into the water, which drives up corrosion activity.

2. Fouling tends to increase, because the formation of Fe_3O_4 and other iron oxide compounds are promoted with O_2 in the system.

c) Temperature.

1. Water is more likely to exist as a liquid in lower-temperature process streams. Therefore, oxygenated water corrosion tends to be prevalent in cooler services.

2. Water has a higher solubility for oxygen at lower temperature, so higher levels of oxygen can dissolve into cooler water. The greater oxygen content leads to increased corrosion rates. Corrosion rates generally increase with temperature, but in this case, as the temperature increases, the solubility of oxygen in the water decreases, thus offsetting the effect of temperature.

d) High velocity and turbulence.

1. When velocity increases beyond 10 fps (3 m/s) and/or turbulence increases, non-boiler oxygen pitting and corrosion increase. Interference with the formation of protective iron oxides promotes corrosion on fresh metal surfaces.

3.49.4 Affected Units or Equipment

a) If a separate water phase is present, oxygenated water corrosion is typically found along the bottom of the piping system.

b) In a system that is only water wetted, oxygenated water corrosion is typically found along the top of the piping system if localized condensation is occurring.

c) Any turbulent areas immediately downstream of weld protrusions, piping misalignment, elbows, and penetrations in the piping can experience accelerated corrosion. If flow is two phase, more aggressive

corrosion may occur in the vapor space as the velocity of the vapor is typically higher than the velocity of the liquid.

1. Preferential weld corrosion may occur in some welds.

d) Small-bore connections that are exposed to low or no flow and are in wetted service with O_2 present may experience oxygenated water corrosion. Vents at a water/vapor interface (if one exists) and drains that extend beyond insulation and create a cooling fin are particularly vulnerable.

e) Vacuum units are subject to oxygenated water corrosion because O_2 enters vacuum unit systems through leaking valve packing, flanges, seals, or undetected thru-wall corrosion. Only small amounts of O_2 are required for a significant increase in oxygenated water pitting rates. The highest corrosion rates are in vacuum systems that use steam ejectors to produce the vacuum. Oxygenated water corrosion can be found where steam condenses in the ejector coolers, in the SW system, and at the interface in the piping and exchanger shells.

f) O_2 that makes it through the vacuum system can potentially end up in downstream light ends units, including the flare gas recovery unit. Oxygenated water corrosion appears in any location where water may accumulate, such as compressor inlet piping low points and the piping off suction knockout drums.

3.49.5 Appearance or Morphology of Damage

Oxygenated water corrosion appears as extensive general pitting on wetted surfaces. Localized pitting occurs in low-velocity areas at reduced temperatures. If high velocities [≥10 fps (>3 m/s)] are an issue, localized accelerated corrosion appears where Fe_3O_4 is absent, at the back side of elbows, or where turbulence may occur, such as downstream of valves.

3.49.6 Prevention/Mitigation

a) The key to avoiding oxygenated water corrosion is to limit the amount of O_2 within the non-aerated systems. Keeping O_2 out of the system reduces corrosion rates dramatically. If O_2 enters the system, expect corrosion activity to significantly increase. Decreasing the amount of O_2 in the system can be achieved by limiting in-leakage of air through the sources described above in 3.49.4.

1. When O_2 concentration below 20 ppb is achieved, carbon and low-alloy steels are the preferred material.

2. The use of oxygen scavenger injection can also be considered for non-aerated systems to reduce O_2 concentration. However, this is generally not recommended unless vacuum leaks cannot be eliminated.

b) A filming amine corrosion inhibitor can be added to reduce corrosion in non-aerated systems. It is important to ensure the filming amine selected does not have an adverse effect on the process. Note that the overall effectiveness of the inhibitor should be proven through subsequent inspection and monitoring. Using inhibitors is generally not recommended unless vacuum leaks cannot be eliminated.

c) Use internal vessel coatings to limit the damage from oxygenated water corrosion. The coating system needs to be is designed for the service and the system in which the coating is to be applied. The temperature guidelines for the specific coating need to be followed.

3.49.7 Inspection and Monitoring

a) Oxygenated water corrosion is typically localized, so inspection plans and practices need to take this into account. The focus should be on high-velocity and turbulent areas and stagnant or low-flow areas.

1. Both straight run piping and fittings can be affected. The full circumference of piping and components should be inspected.

2. Specific areas to check include downstream of ejectors, control valves, throttled valves, pumps, flow orifices, and internal protrusions, as well as at elbows, tees, and reducers.

3. Check the top of piping where condensing conditions exist.

4. Check the bottom of piping and small-bore connections where a separate water phase or cooler conditions exist.

5. Check the water/vapor interface, if one exists.

b) RT, manual UT scanning or grid UT, and AUT are suitable NDE methods.

c) Permanently mounted thickness monitoring sensors can be used.

d) O_2 content less than 100 ppb in non-aerated water systems is very difficult to measure, so consult a specialist, as needed, to ensure the correct procedures for sampling and monitoring the water are used.

3.49.8 Related Mechanisms

Cooling water corrosion (3.20), boiler water and condensate corrosion (3.9), brine corrosion (3.10), and concentration cell corrosion (3.19).

3.49.9 References

1. *ASM Metals Handbook*, ASM International, Materials Park, OH, 1985, p. 4.91.

2. M.G. Fontana, *Corrosion Engineering*, Third Edition, 1987, p. 17.

3. K.L. Heidersbach, “Hungry Water Corrosion Testing,” Chevron Corp. Energy Technology Company, 2011.

4. N. Fredj, T.D Burleigh, K L. Heidersbach, and B.R. Crowder, “Corrosion of Carbon Steel in Waters of Varying Purity and Velocity,” Paper No. 1461, *Corrosion/2012*, NACE International, Houston, TX.

3.50 Phenol (Carbolic Acid) Corrosion

3.50.1 Description of Damage

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

3.50.2 Affected Materials

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

3.50.3 Critical Factors

a) Temperature, water content, alloy chemistry, and flow velocity are the critical factors.

b) The corrosion rate of carbon steel at temperatures less than 212 °F (100 °C) is typically 1 mpy to 2 mpy.

c) The corrosion rate of carbon steel exceeds 20 mpy above 350 °F (175 °C).

d) Carbon steel and 304/304L stainless steel corrode rapidly in phenol service above 500 °F (260 °C).

e) Dilute aqueous solutions (5 % to 15 % phenol) can be very corrosive.

f) High velocities may promote localized corrosion (i.e. erosion-corrosion), particularly at velocities greater than 30 ft/s.

3.50.4 Affected Units or Equipment

a) Phenol extraction facilities in lube oil plants.

1. Corrosion is usually minimal in the treating section when the temperature is below 250 °F (121 °C).
2. Corrosion can occur in the recovery section where spent phenol is separated by vaporization.
3. Sulfur and organic acids may lead to naphthenic acid attack and sulfidation in the hot extract circuit.
4. Dilute aqueous solutions (5 % to 15 % phenol) are very corrosive to the extract dryer condensers.
5. Erosion-corrosion and/or condensation corrosion may be observed in tower overhead circuits.

3.50.5 Appearance or Morphology of Damage

a) Corrosion will be general or localized, with local corrosion often being the result of erosion-corrosion.

3.50.6 Prevention/Mitigation

a) Corrosion is best prevented through proper materials selection and control of phenol solvent chemistry.

b) Velocity in carbon steel should be limited to less than 30 ft/s

c) Overhead piping circuits should be designed for a maximum velocity of 30 fps in the recovery section.

d) Recovery tower overhead temperatures should be maintained to at least 30 °F (15 °C) above the dew point.

e) Type 316L stainless steel may be effective in the top of the dryer tower, phenol flash tower, and various condenser shells and separator drums that handle phenol-containing water.

f) Tubes and headers in extract furnaces should be 316L.

g) Alloy C276 has been used in areas of high velocity or other locations where 316L is inadequate.

3.50.7 Inspection and Monitoring

a) VT can be used for accessible internal surfaces at liquid impingement and turbulent flow areas and is often followed up with UT thickness measurements in suspect areas.

b) External UT can be used to identify, map, and monitor loss in thickness.

c) RT, where practical considering pipe diameter, can be effective for identifying localized attack.

d) Permanently mounted thickness monitoring sensors can be used.

e) ER corrosion probes and corrosion coupons have been used for corrosion monitoring.

3.50.8 Related Mechanisms

Erosion/erosion-corrosion (3.27).

3.50.9 References

1. J. Gutzeit, R.D. Merrick, and L.R. Scharfstein, “Corrosion in Petroleum Refining and Petrochemical Operations,” *Metals Handbook*, Volume 13, ASM International, Materials Park, OH, 1987, pp. 1262–1287.

3.51 Phosphoric Acid Corrosion

3.51.1 Description of Damage

Phosphoric acid is most often used as a catalyst in polymerization units. It can cause corrosion of carbon steel, depending on water content. Corrosion is typically localized to where the conditions for causing corrosion exist.

3.51.2 Affected Materials

For materials typically used or considered for this application, the order of increasing resistance is carbon steel, 304L SS, 316L SS, Alloy 20, and Alloy 825. The “L” (low carbon content) grades of stainless steels are preferable to straight grades to reduce the risk of sensitization and intergranular corrosion.

3.51.3 Critical Factors

a) Acid concentration, water content (i.e. the presence of water), temperature, and contaminants are the critical factors.

b) Solid phosphoric acid catalysts are not corrosive to carbon steel unless free water is present. When water is present, severe corrosion of carbon steel may occur.

   1. A small amount of water in contact with the catalyst can create a very concentrated (non-diluted) acid.

   2. Corrosion can penetrate a ¼-in. (6-mm) thick steel tube in 8 hr.

c) Corrosion rates increase with increasing temperature.

d) Contaminants such as chlorides, fluorides, and other halide salts can increase phosphoric acid corrosion rates.

e) Most corrosion probably results from water washing operations during shutdowns.

f) Low points that may collect water are subject to localized corrosion.

3.51.4 Affected Units or Equipment

a) Piping and equipment in polymerization units where water mixes with catalyst.

b) Corrosion is usually found in low points and low-velocity areas where there is little or no circulation. Examples include piping manifolds, bypass lines, dead-legs, partial penetration welds, the bottom of kettle-type reboilers, and exchangers where there is sufficient residence time to permit the settling of acid droplets.

3.51.5 Appearance or Morphology of Damage

The corrosion mainly occurs as localized thinning with either a pitted or more general (smoother) appearance on the attacked carbon steel surface. Sensitized stainless steel will suffer intergranular corrosion.

3.51.6 Prevention/Mitigation

a) Water content (i.e. moisture content) should be limited to less than 400 ppm.

b) Where water cannot be eliminated, selective upgrading to corrosion-resistant materials is the practical option.

c) Type 304L SS is satisfactory for phosphoric acid concentration of 100 % up to about 120 °F (50 °C). Type 316L SS is required from 120 °F to 225 °F (50 °C to 105 °C).

d) Type 316L SS and Alloy 20 are effective at concentrations up to 85 % at boiling temperatures.

e) At even higher temperatures above boiling, where the liquid acid is still present, Alloy 825 may be needed.

3.51.7 Inspection and Monitoring

a) UT and RT can be used to detect and measure loss of thickness.

b) Permanently mounted thickness monitoring sensors can be used.

c) The water from the first column overhead receiver should be monitored for iron content. In addition, it is advisable to monitor temperatures, pH, water content (e.g. by installing a moisture analyzer), and for phosphoric acid carryover past the reactor.

d) Online corrosion monitoring can be performed using ER probes and/or corrosion coupons in the water draw from the first column overhead condenser and the reboiler.

3.51.8 Related Mechanisms

Although corrosion is caused by a number of strong and weak acids in the refining industry, phosphoric acid corrosion is specific to polymerization units. Where caustic neutralization is employed in polymerization units, if the resulting salts are not properly separated out, wet, corrosive solids may deposit and cause under-deposit corrosion. (See 3.19.)

3.51.9 References

1. R.A. White and E.F. Ehmke, *Materials Selection for Refineries and Associated Facilities*, NACE International, Houston, TX.

2. *Corrosion Control in the Refining Industry*, NACE Course Book, NACE International, Houston, TX, 1999.

3.52 Polythionic Acid Stress Corrosion Cracking

3.52.1 Description of Damage

a) Intergranular SCC that can occur in sensitized austenitic stainless steels and some Ni alloys (Alloy 800 and Alloy 600) when sulfide scale formed on the surface during operation is exposed to air and moisture. The combination of sulfide scale, air (i.e. oxygen), and moisture creates sulfur acids on the surface that then cause polythionic acid stress corrosion cracking (PTA SCC). It normally occurs during shutdowns or start-ups.

b) Usually occurs adjacent to welds or in high-stress areas.

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

3.52.2 Affected Materials

Austenitic stainless steels (300 series SS) and austenitic alloys (Alloy 600/600H and Alloy 800/800H/800HT). Alloys 625 and 825 are also susceptible but require extended periods at much higher temperatures [>1200 °F (650 °C)] to sensitize.

3.52.3 Critical Factors

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

1. Environment—Susceptible metals form a surface sulfide scale when exposed to sulfur compounds in a high-temperature reducing process environment. The scale may then react with air (oxygen) and moisture to form sulfur acids (polythionic acids, $H_2S_xO_6$).

2. Material—The material must be susceptible to sensitization and in a sensitized condition.

3. Tensile Stress—The stress can be residual or applied.

b) Affected alloys become sensitized during exposure to elevated temperatures during manufacture, welding, or high-temperature service. Sensitization refers to the composition/time/temperature-dependent formation of chromium carbides in the grain boundaries of the metal. Sensitization occurs in the 700 °F to 1500 °F (370 °C to 815 °C) temperature range. However, chemically stabilized grades of stainless steel, e.g. Types 321 and 347, can withstand service temperatures greater than 700 °F without suffering detrimental sensitization. Some refiners permit the use of these alloys at temperatures substantially greater than 700 °F without requiring thermal stabilization.

c) The carbon content and the thermal history of the alloy have a significant effect on sensitization susceptibility. Regular and high carbon grades of stainless steels such as Types 304/304H and 316/316H are particularly susceptible to sensitizing in the weld HAZ. Low carbon “L” grades (<0.03 % C) are less susceptible and usually can be welded without sensitizing. The L grades will not sensitize provided long-term operating temperatures do not exceed about 750 °F (400 °C).

d) Residual tensile stresses in most components, especially in non-stress-relieved welds, are usually sufficient to promote cracking and are the most common source of the tensile stress needed to cause cracking.

3.52.4 Affected Units or Equipment

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

b) Fired heaters burning oil, gas, coke, and most other sources of fuel may be affected depending on sulfur levels in the fuel and combustion conditions in the firebox. (Fuel-rich conditions will favor formation of sulfide scales instead of oxide scales.) In places where there are environmental restrictions on the burning of high sulfur fuels, the occurrences of fire-side PASCC have diminished.

c) FCC Units—Air rings, plenums, slide valves, cyclone components, expansion joint bellows, and piping.

d) Hydroprocessing Units—Heater tubes, hot feed/effluent exchanger tubes, pressure vessels (including heat exchangers and reactors), piping, and bellows.

e) Crude and Coker Units—Heater tubes and piping.

f) Boilers and other high-temperature equipment exposed to sulfur-containing combustion products can also be susceptible if sensitized alloys are involved.

3.52.5 Appearance or Morphology of Damage

a) Typically occurs next to welds (Figure 3-52-1 and Figure 3-52-4) but can also occur in the base metal. It is usually quite localized and may not be evident until a leak appears during start-up or, in some cases, operation.

b) Cracking propagates intergranularly. (Figure 3-52-2 and Figure 3-52-5)

c) Corrosion or loss in thickness is usually negligible.

3.52.6 Prevention/Mitigation

a) If potentially susceptible equipment will be opened or exposed to air, preventive measures should be taken to minimize or eliminate PTA SCC. These include (i) flushing the equipment during or immediately after shutdown with alkaline or soda ash solution to neutralize the acids formed after shutdown and exposure to air and moisture or (ii) purging with dry nitrogen or nitrogen/ammonia during the shutdown to prevent air exposure and the formation of polythionic acids. Refer to guidelines in NACE SP0170.

b) Furnace tubes that have coke on the tube ID should undergo some form of decoking process prior to or concurrent with the alkaline washing if the tube IDs will be exposed to air. Alkaline washing with coke present has low effectiveness. Refer to NACE SP0170 for guidance.

c) Keeping the firebox heated above the dew point to prevent acids from forming on the heater tube internal surfaces, if practical, will also prevent PTA SCC. This can also be accomplished by using dehumidification equipment to reduce the water dew point inside the tubes below ambient.

d) Low carbon grades of stainless steel such as 304L, 316L, and 317L provide some measure of improvement over higher carbon grades. The L grades will sensitize if exposed more than several hours above about 1000 °F (540 °C) or long-term above 750 °F (400 °C).

e) Improved resistance to PTA SCC cracking can be achieved with chemically stabilized versions of these alloys containing small amounts of titanium (Ti) or niobium (Nb) and tantalum (Ta). [Note that niobium was also called columbium (Cb), but niobium is now the generally accepted name.] Types 321 and 347 SS are the chemically stabilized grades of austenitic stainless steel most commonly used. Alloy 20Cb-3 as well as Alloys 825 and 625 are also chemically stabilized.

f) Supplemental requirements in ASTM specifications provide for mill products to be delivered in a thermally stabilized condition rather than simply solution annealed. This heat treatment will minimize potential sensitization problems at higher temperatures, e.g. as found in a heater.

g) A thermal stabilization heat treatment at 1650 °F (900 °C) may be applied to chemically stabilized austenitic stainless steel welds after all welding is complete to reduce sensitization and PTA SCC susceptibility at the welds. This heat treatment is also applied after welding material that was thermally stabilized in the mill in order to restore the thermal stabilization destroyed by the heat of welding.

h) The degree of sensitization and resultant susceptibility to PTA SCC can be determined by laboratory corrosion testing according to ASTM A262 Practice C. This test is also used as a quality control check at the

mill on chemically stabilized grades, with a sensitizing heat treatment applied prior to testing in order to assess resistance to sensitization.

3.52.7 Inspection and Monitoring

a) PTA SCC is most effectively managed by prevention rather than through inspection. PTA SCC can be an inspection challenge because the cracking may not occur until well into a turnaround.

b) Monitoring for PTA SCC cracking during operation is not effective. Conditions causing the cracking are not usually present while the unit is online.

c) PT examination is the most common method used to detect PTA SCC. (Figure 3-52-1 and Figure 3-52-3) However, because the cracks are filled with a tight deposit, flapper wheel sanding or grinding may be needed to improve the PT sensitivity.

d) ECT can detect surface cracks on the crack initiation side.

e) AET has had some success in detecting and locating PTA SCC. However, results sometimes can be inconclusive, and quality AET data may be difficult to obtain.

f) Angle beam UT (SWUT and PAUT) crack detection techniques may be useful depending on thickness, metallurgy, and accessibility considerations and limitations.

g) FMR can be used to determine the degree and extent of sensitization.

3.52.8 Related Mechanisms

Intergranular corrosion and intergranular attack.

3.52.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH, p. 327.

2. NACE SP0170, *Protection of Austenitic Stainless Steels and Other Austenitic Alloys from Polythionic Acid Stress Corrosion Cracking During a Shutdown of Refinery Equipment*, NACE International, Houston, TX.

3. D.V. Beggs, and R.W. Howe, “Effects of Welding and Thermal Stabilization on the Sensitization and Polythionic Acid Stress Corrosion Cracking of Heat and Corrosion-resistant Alloys,” Paper No. 541, *Corrosion/93*, NACE International, Houston, TX.

4. L. Scharfstein, “The Effect of Heat Treatments in the Prevention of Intergranular Corrosion Failures of AISI 321 Stainless Steel,” *Materials Performance*, September 1983, pp. 22–24.

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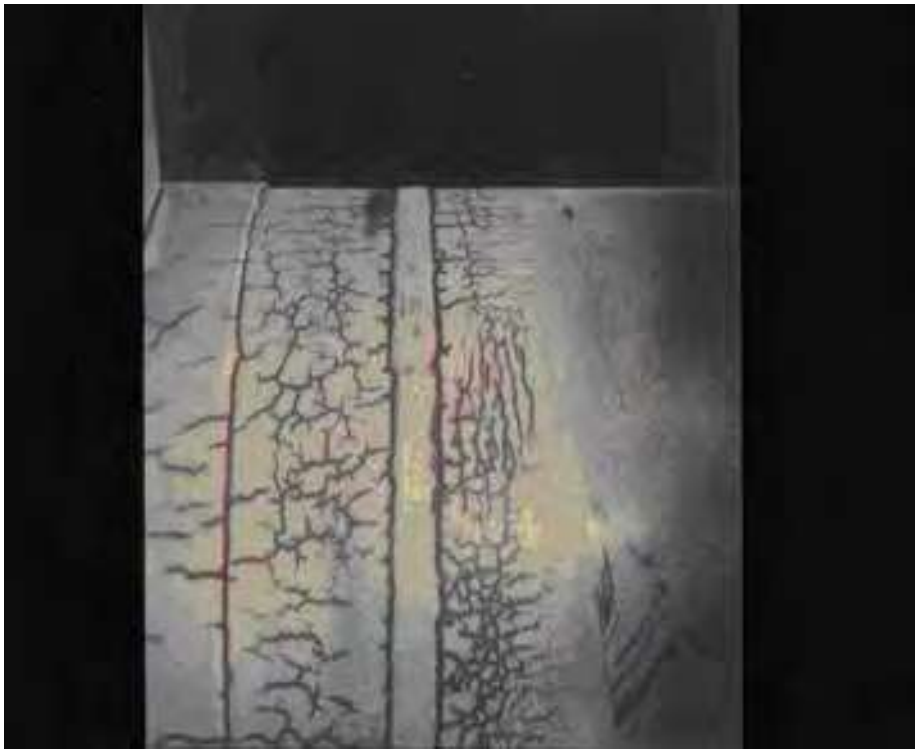

Figure 3-52-1—Dye penetrant (PT) inspection showing extensive OD PTA SCC around welds.

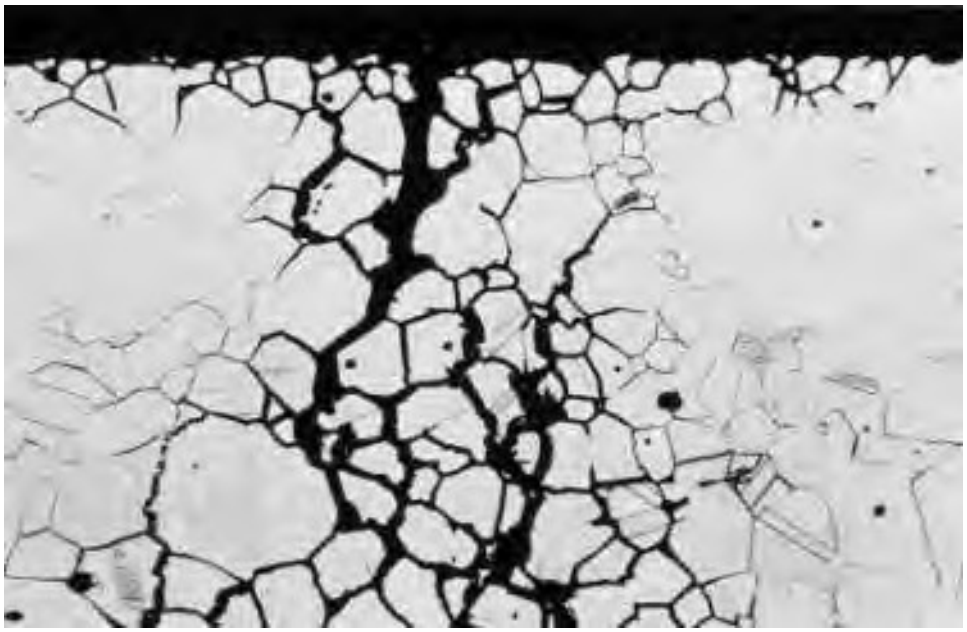

Figure 3-52-2—High-magnification photomicrograph of metallographic sample showing intergranular cracking and grain dropping.

Figure 3-52-3—PT inspection of a Type 304 stainless steel catalyst withdrawal line piping and weld neck flange.

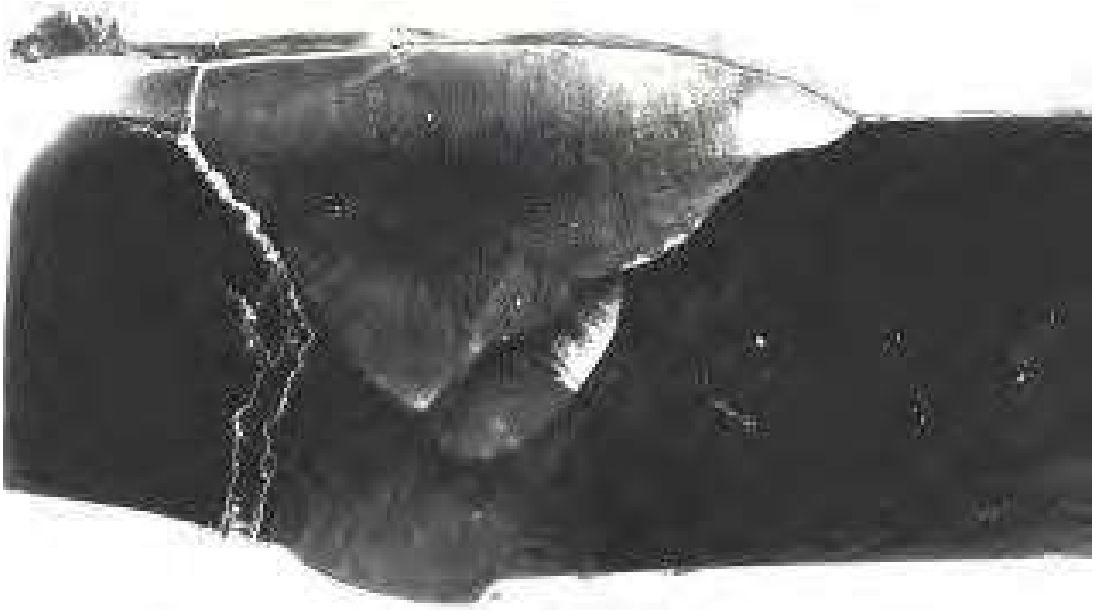

Figure 3-52-4—Cross section of the catalyst withdrawal line attached to the flange in Figure 3-50-3 showing cracking in the weld HAZ. Magnification 3X.

Figure 3-52-5—Higher-magnification view showing intergranular cracking. Magnification 200X.

3.53 Refractory Degradation

3.53.1 Description of Damage

Both thermally 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. High skin temperatures on the base metal being protected may result from refractory damage.

3.53.2 Affected Materials

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

3.53.3 Critical Factors

a) Refractory design, selection, and installation are the keys to minimizing damage. Anchor materials need to be selected properly. Process environment factors are also critical.

b) Refractory lined equipment should be designed to handle the erosion, thermal shock, and thermal expansion to be encountered in service.

c) Refractory type and density need to be selected to resist abrasion and erosion based on service requirements.

d) Needles and other fillers need be compatible with the process environment composition and temperature.

e) Dryout schedules, cure times, and application procedures should be in accordance with the manufacturer's specifications and the appropriate ASTM requirements.

f) Anchor materials need to be compatible with the thermal coefficient of expansion of the base metal.

g) Anchors need to be resistant to oxidation in high-temperature services.

h) Anchors need to be resistant to condensing sulfurous acids in heaters and flue gas environments.

i) In erosive services, refractory may be washed away or thinned, exposing the anchoring system. (Figure 3-53-1)

j) Coke deposits may develop behind refractory and promote cracking and deterioration.

k) Refractories can suffer vibration damage.

l) Refractories can be damaged by exposure to moisture.

3.53.4 Affected Units or Equipment

a) Refractories are extensively used in FCC reactor regenerator vessels, piping, cyclones, slide valves, and internals.

b) Refractories are also used in fluid coker units, in cold shell catalytic reforming reactors, and in waste heat boilers and thermal reactors in sulfur plants.

c) Boiler and heater fireboxes, floors, and stacks that use refractory are also affected.

3.53.5 Appearance or Morphology of Damage

a) Refractory may show signs of excessive cracking, spalling or lift-off from the substrate, softening, or general degradation.

b) A potential warning sign of vibration damage to refractories is visible damage and failure of the refractory or the anchoring system.

3.53.6 Prevention/Mitigation

a) Proper selection, design, and installation of refractory, anchors, and fillers are the keys to minimizing refractory damage and failure.

b) Operating parameters should be monitored to identify process upsets (e.g. temperature excursions or loss of flame) and cyclic operation that may impact the integrity and effectiveness of the refractory lining. Refractory degradation should be taken into account as a potential damage mechanism when selecting IOWs.

3.53.7 Inspection and Monitoring

a) Refractory and ferrules (tubesheets) should be visually inspected looking for signs of chemical degradation or mechanical degradation (e.g. spalling, slumping, or cracking of ferrules) during equipment outages.

b) For FCC vessels, hammer testing can be used in areas known for channeling behind the refractory.

c) Cold-wall equipment can be surveyed while onstream using IR thermography, or at least VT where temperature indicating paint has been applied or where paint is badly discolored or burnt, to monitor for hot spots and help identify potential refractory damage.

3.53.8 Related Mechanisms

Oxidation (3.48), sulfidation (3.61), flue gas dew point corrosion (3.29), HTHA (3.36), decarburization (3.25), carburization (3.13), and metal dusting (3.44).

3.53.9 References

1. R.A. White and E.F. Ehmke, *Materials Selection for Refineries and Associated Facilities*, NACE International, Houston, TX, 1991, pp. 33, 57.

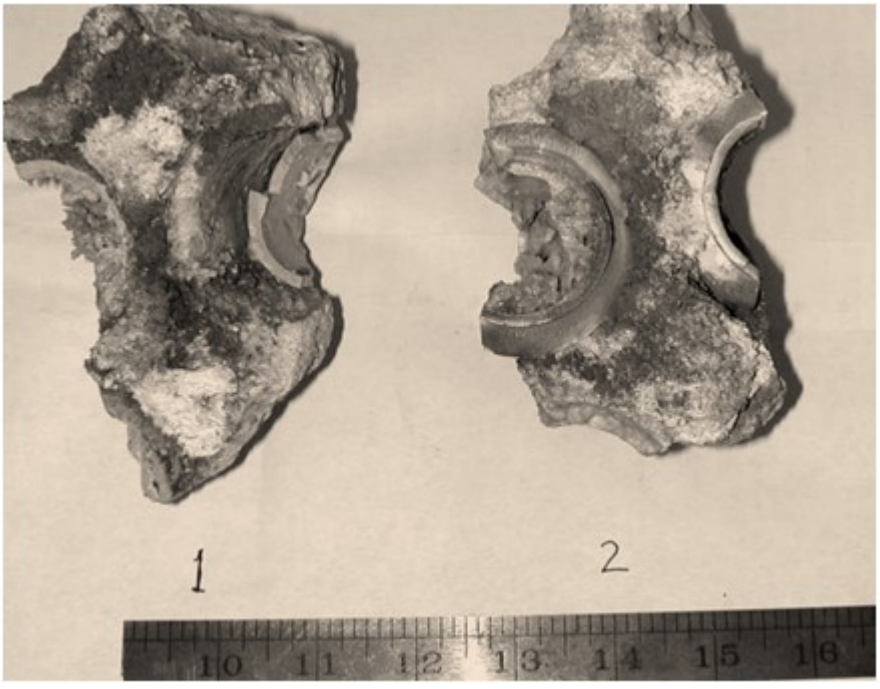

Figure 3-53-1—Damaged refractory and ferrules.

3.54 Stress Relaxation Cracking (Reheat Cracking)

3.54.1 Description of Damage

Cracking of a metal due to stress relaxation via grain boundary strain in the creep temperature range during PWHT or in service at elevated temperatures. The temperature above which it occurs depends on the type of alloy. It is most often observed in heavy wall sections. At various times and in various situations, stress relaxation cracking (SRC) has also been called reheat cracking, stress-relief cracking, creep embrittlement, low creep ductility cracking, stress-induced cracking, and stress-assisted grain boundary oxidation cracking.

3.54.2 Affected Materials

a) Cr-Mo steels, especially 2¼Cr-1Mo steel with vanadium added, 1Cr-½Mo, and 1¼Cr-½Mo.

b) Types 304H, 316H, 321, and 347 SS.

c) Nickel-based alloys, particularly Alloy 800H, 800HT, Alloy 617, and centrifugally cast 22Cr-35Ni-Nb used for heavy wall piping and headers in hydrogen reformer heaters.

d) HSLA steels are very susceptible.

3.54.3 Critical Factors

a) In addition to exposure to elevated temperature in the creep range, important parameters include the type of material (chemical composition, impurity elements), grain size, weld metal and base metal strength, residual stresses from fabrication (cold working, welding), section thickness (which controls restraint and stress state), notches and stress concentrators, and welding and heat treating applied.

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

   1. The affected alloys contain alloying additions that promote fine intragranular precipitate particles that make the grains stronger than the grain boundaries and force the creep deformation to be concentrated at the grain boundaries.

   2. Impurity elements like phosphorous, tin, antimony, and arsenic, if present, also promote SRC, particularly in Cr-Mo low-alloy steels, because they concentrate at grain boundaries and limit grain boundary ductility.

c) SRC 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.

d) The approximate temperatures above which, or ranges within which, SRC occurs for different types of alloys are as follows:

   1. 2¼Cr-1Mo-V: 840 °F (450 °C);

   2. 1Cr-½Mo and 1¼Cr-½Mo: 900 °F (480 °C);

   3. Types 347, 321, and 304H SS: 930 °F (500 °C) to 1380 °F (750 °C); and

   4. nickel-based alloys: 930 °F (500 °C) to 1380 °F (750 °C)

e) SRC is normally more prevalent where large grain size exists, particularly in the low-alloy steels, e.g. in the coarse-grained HAZ. Large grain size means less total grain boundary volume to accommodate the creep strain, i.e. the creep strain is concentrated in a relatively small grain boundary volume.

f) SRC requires the presence of high stresses and is therefore more likely to occur in thicker sections and higher-strength materials, including higher strength resulting from original plate mill heat treatments as in the case of 1Cr-½Mo and 1¼Cr-½Mo steel grades.

g) Stress relief and stabilization heat treatment of Types 321 and 347 SS for maximizing Cl^- SCC and/or PASCC resistance can cause SRC problems, particularly in thicker sections.

h) In the first half of 2008, numerous cases of SRC, primarily referred to as reheat cracking, occurred during 2¼Cr-1Mo-V reactor fabrication. The cracks were in weld metal only, transverse to the welding direction, and in only submerged-arc welding (SAW) welds. It was traced to a contaminant in the welding flux. A weld material screening test has since been implemented, as described in API 934-A.

3.54.4 Affected Units or Equipment

a) Catalytic reformer and FCC units.

1. Hot-wall 1Cr-½Mo and 1¼Cr-½Mo vessels and piping operated above 900 °F (480 °C), especially at the toe of nozzle-to-shell welds and reinforcement pads or wherever there is high restraint or high stress concentrations, including high pipe loads on pipe circumferential welds. “Peaking” greater than $^1/_{16}$ in. (1.6 mm) in the longitudinal weld seams of welded pipe also increases the likelihood of SRC.

2. This cracking has also been referred to as low creep ductility cracking and creep embrittlement cracking.

b) Hydroprocessing.

1. SRC can occur in heavy wall Type 321 and 347 SS effluent piping during fabrication PWHT, e.g. postweld stabilization heat treatment, or when welding is performed after being in service.

2. Type 321 and 347 SS outlet piping from the recycle hydrogen heater to the reactor inlet line can operate hot enough to be susceptible to SRC during operation.

3. Cracking can occur in Cr-Mo heavy wall reactor vessels during fabrication.

c) Hydrogen manufacturing units.

1. SRC has occurred in stainless steel tubes and piping in units that have a preconverter and a feed preheat coil.

2. SRC has occurred in stainless steel and Alloy 800H steam superheater tubes.

d) High-pressure steam piping.

1. 1Cr-½Mo and 1¼Cr-½Mo piping operating above 900 °F (480 °C) with circumferential welds having significant stress risers and high applied loads.

3.54.5 Appearance or Morphology of Damage

a) SRC 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 HAZ; however, it can also occur in weld deposits. (Figure 3-54-1 to Figure 3-54-4)

b) In many cases, cracks initiate at some type of stress concentration. Once initiated, SRC cracks can enable further propagation by fatigue cracking.

3.54.6 Prevention/Mitigation

a) Joints and nozzles in 1Cr-½Mo and 1¼Cr-½Mo vessels and piping, especially heavy wall sections, should be designed to minimize stress concentration as well as restraint during welding and PWHT. Adequate preheat must also be applied.

b) 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 fit-up problems or by "peaking" due to the plate edges not being properly rolled.

c) Metallurgical notches arising from the welding operation are frequently the cause of cracking at the boundary between the weld and the HAZ.

d) For 1Cr-½Mo and 1¼Cr-½Mo vessels operating above 900 °F (480 °C), follow the material grade and PWHT temperature guidelines in API 934-E.

e) For 2¼Cr-1Mo-V welds, consider the recommendations for welding material screening tests in API 934-A.

f) For thick-wall Type 321 or 347 SS piping, consider the possibility of SRC in deciding whether to PWHT. Also, minimize constraint, pipe loads, and stress concentrations at welds.

g) 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 %.

h) For Alloy 800H and 800HT, which will operate at >1000 °F (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 or 800HT filler material and should be stress relieved. Refer to UNF-56(e) in ASME *BPVC* Section VIII, Division 1 and to API 942-B for additional information.

i) Low heat input welding procedures help minimize grain coarsening in the HAZ.

j) Heating rates at temperatures above 480 °F (250 °C) should generally comply with the limits provided by ASME *BPVC* Section VIII for PWHT.

3.54.7 Inspection and Monitoring

a) For Cr-Mo steels, surface cracks can be detected with WFMT, MT, or PT.

b) For Type 321 and 347 SS as well as the nickel-based alloys, PT or angle beam UT (SWUT or PAUT) examination can be used to detect cracks.

c) Special procedures, equipment, and interpretation are often required for angle beam UT inspection of austenitic materials with a thickness greater than $^{3}/_{4}$ in. (19 mm) compared to similar thickness non-austenitic materials.

d) Embedded cracks can only be found by UT examination.

e) Inspection for cracking in 2¼Cr-1Mo-V reactors during fabrication is typically done with TOFD and/or angle beam UT (SWUT or PAUT), with the demonstration block having defects as small as 3-mm side-drilled holes, as described in API 934-A.

3.54.8 Related Mechanisms

Creep and stress rupture (3.23). SRC has also been referred to as reheat cracking, stress-relief cracking, creep embrittlement, low creep ductility cracking, stress-induced cracking, and stress-assisted grain boundary oxidation cracking.

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13. API Recommended Practice 934-E, *Recommended Practice for Materials and Fabrication of 1¼Cr-½Mo Steel Pressure Vessels for Service Above 825 °F (440 °C)*, American Petroleum Institute, Washington, DC.

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Figure 3-54-1—Samples removed from a cracked 12-in. NPS Type 321 SS elbow in a hot recycle H_2 line that operated at 985 °F (530 °C) in a hydrocracker.

Figure 3-54-2—Crack at weld from Type 321 SS elbow shown in Figure 3-52-1.

Figure 3-54-3—Cross section through the weldment showing the crack in Figure 3-52-2.

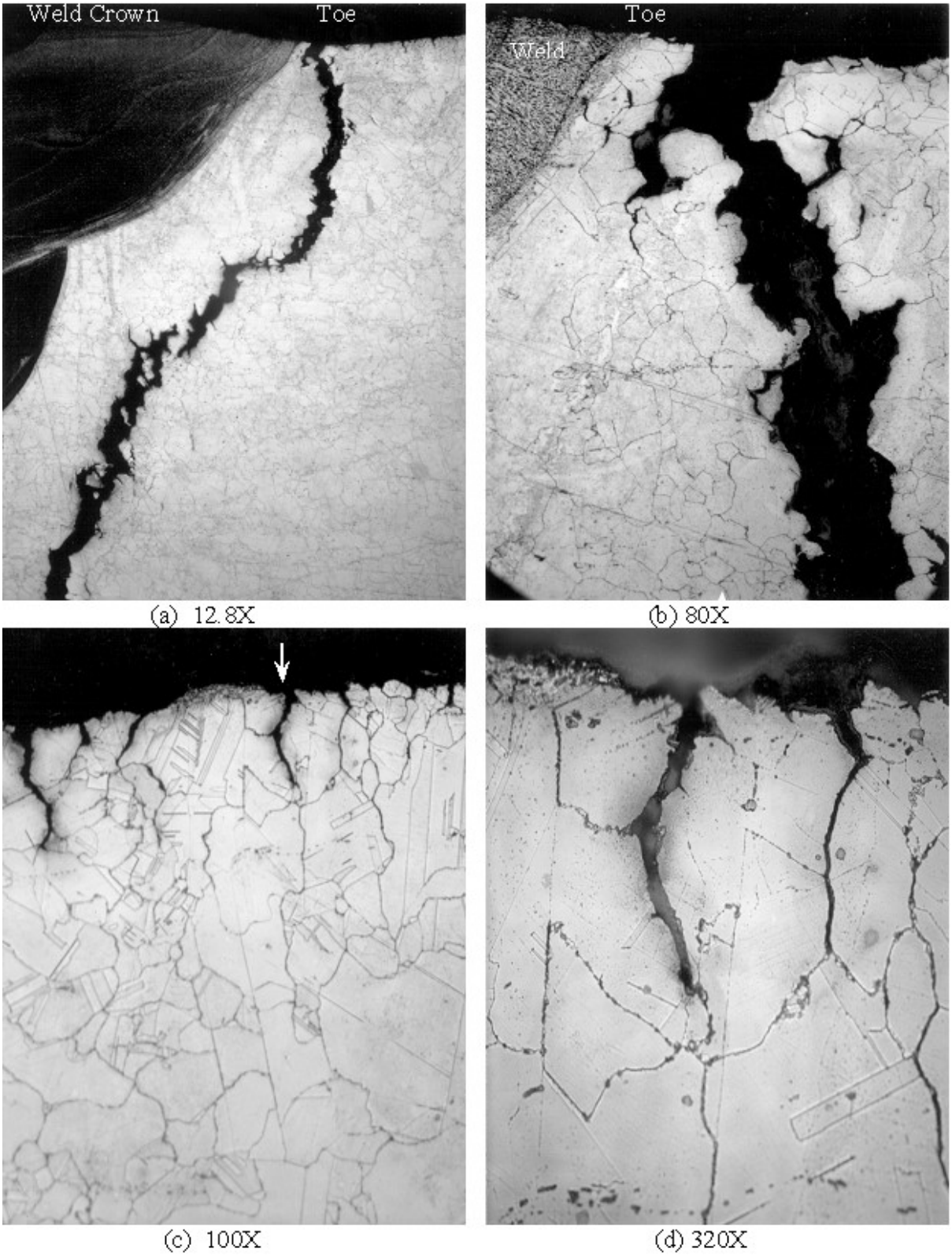


Figure 3-54-4—Photomicrographs of the weldment area shown in Figure 3-52-3.

3.55 Short-term Overheating—Stress Rupture (Including Steam Blanketing)

3.55.1 Description of Damage

Permanent deformation occurring at very high temperatures and typically relatively low stress levels as a result of localized overheating. It typically will result in bulging and eventual failure by stress rupture. If the temperature is high enough, failure will occur very quickly by tensile overload, since tensile strengths drop off dramatically at very high temperatures. At less severe temperatures, short-term creep failure will occur.

3.55.2 Affected Materials

All fired heater tube and boiler tube materials and common materials of construction.

3.55.3 Critical Factors

a) Temperature, time, and stress are the critical factors.

b) In heaters, it is usually due to flame impingement or any other cause of local overheating.

c) In boiler tubes, it is due to steam blanketing (DNB), which may result from flame impingement or restricted water flow.

d) The higher the internal pressure or loading, the shorter will be the time to failure. However, bulging and distortion can be significant even at low pressures and stresses if the temperature is high enough.

e) The local overheating is well above the design temperature.

f) Previous loss in thickness due to corrosion will reduce time to failure due to the increased stress on the remaining thickness.

3.55.4 Affected Units or Equipment

a) All fired heater tubes are susceptible.

b) Heaters with coking tendencies such as in crude, vacuum, heavy oil hydroprocessing, and coker units are often fired harder to maintain heater outlet temperatures and are thereby more susceptible to localized tube overheating. Flame impingement can also lead to localized overheating.

   1. Steam-air decoking can also create localized hot spots internally if the coke is burned out too aggressively.

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

d) Hydroprocessing reactors may be susceptible to localized overheating of reactor beds due to inadequate hydrogen quench or flow maldistribution.

e) Catalytic reforming reactors may be susceptible to localized overheating due to coking of the catalyst.

f) Refractory lined equipment in an FCC unit, sulfur plant, H_2 manufacturing plant, and other units may suffer localized overheating due to refractory damage and/or excessive firing.

g) Heater fireboxes can suffer localized overheating due to loss of protective refractory or insulation.

3.55.5 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) Tube ruptures are characterized by open “fishmouth” failure and are usually accompanied by a thin, knife-edged fracture surface resulting from the excessive deformation and bulging prior to failure. (Figure 3-55-1 to Figure 3-55-5)

c) The microstructure of ruptured tubes will show severe elongation of the grains at the fracture surface due to the plastic deformation that occurs. (Figure 3-55-4)

3.55.6 Prevention/Mitigation

a) Damage can be avoided by minimizing temperature excursions.

b) Proper burner maintenance, management, and fouling/deposit control are needed to minimize hot spots and localized overheating in fired heaters and boilers.

c) Burners that produce a more diffuse flame pattern should be used in heaters.

d) Proper BFW treatment can help prevent some conditions that can lead to restricted flow in boilers.

e) In hydroprocessing equipment, installing and maintaining bed thermocouples in reactors will help minimize the likelihood of hot spots. Proper system design and operation are also important.

f) Refractory in refractory lined equipment should be maintained in serviceable condition.

3.55.7 Inspection and Monitoring

a) Short-term overheating damage or failure can occur in such a short time that inspection as a mitigative or preventive measure may not be possible. However, there are several inspection and monitoring methods applicable to dealing with short-term overheating.

b) Components that are accessible during shutdowns, particularly in fired heaters and boilers, can be visually inspected to find tube bulging, sagging, and other types of deformation. Damage can be quantified by strapping the tubing and taking UT thickness measurements. However, not all components can be checked. Inspection is limited to that which is within line-of-sight, and not all damage is visually apparent.

c) Infrared thermography monitoring of heater tubes for localized hot spots could indicate locations susceptible to short-term overheating failures. This inspection is also limited to line-of-sight locations, but the technique can be employed while the equipment is in operation using either installed or portable IR thermography monitoring tools.

d) Thermocouples can be installed to monitor temperatures of heater tubes as well as other equipment, including refractory lined equipment, during operation. Thermocouples can be attached directly to the metal surface or placed under insulation for approximate temperature measurement. However, thermocouples often cannot identify localized hot spots, because placement of thermocouples often does not coincide with the location of localized hot spots arising later.

e) Refractory damage should be inspected during shutdowns as it may indicate possible short-term overheat damage or may provide clues for where to look for possible tube or other component overheat damage.

f) FMR of accessible components can reveal the microstructure and is used to evaluate creep void formation. With knowledge of operating conditions, FMR may be employed for remaining life assessments of affected components.

g) Steam blanketing that results in long-term localized caustic corrosion (3.14) rather than a short-term overheating failure may be detected by VT of the tube internals using a boroscope.

1. Other localized thinning inspection techniques such as straight beam UT, PAUT, or TOFD can be used, but in the case where the steam generation tubes are finned, these techniques are not applicable.

3.55.8 Related Mechanisms

Creep/stress rupture (3.23) and caustic corrosion/caustic gouging (boilers) (3.14).

3.55.9 References

1. API 579-1/ASME FFS-1, *Fitness-For-Service*, American Petroleum Institute, Washington, DC.
2. API Standard 530, *Calculation of Heater-tube Thickness in Petroleum Refineries*, American Petroleum Institute, Washington, DC.
3. API Standard 660, *Shell-and-Tube Heat Exchangers*, American Petroleum Institute, Washington, DC.
4. *Steam—Its Generation and Use*, 40th Edition, Babcock & Wilcox, 1992.
5. *Combustion: Fossil Power Systems*, Third Edition, Combustion Engineering, Windsor, CT, 1981.
6. H. Thielsch, *Defects and Failures in Pressure Vessels and Piping*, Krieger Publishing, Malabar, FL, 1977.
7. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991.
8. D.N. French, *Metallurgical Failures in Fossil Fired Boilers*, John Wiley and Sons, New York, NY, 1993.
9. B. Dooley and W. McNaughton, *Boiler Tube Failures: Theory and Practice*, 3 Volumes, EPRI, 1995.

Figure 3-55-1—Short-term overheating failure of a vertical, 4.5-in. OD, schedule 160 2¼Cr-1Mo (SA335-P22) hydrocracker radiant tube that was 21 years old. Failure resulted from process-side starvation with the burners running.

Figure 3-55-2—Tube bulged and ruptured due to short-term overheating at a temperature well over 1380 °F (750 °C).

Figure 3-55-3—1Cr-½Mo boiler superheater tube in 700 psig steam service that failed due to overheating.

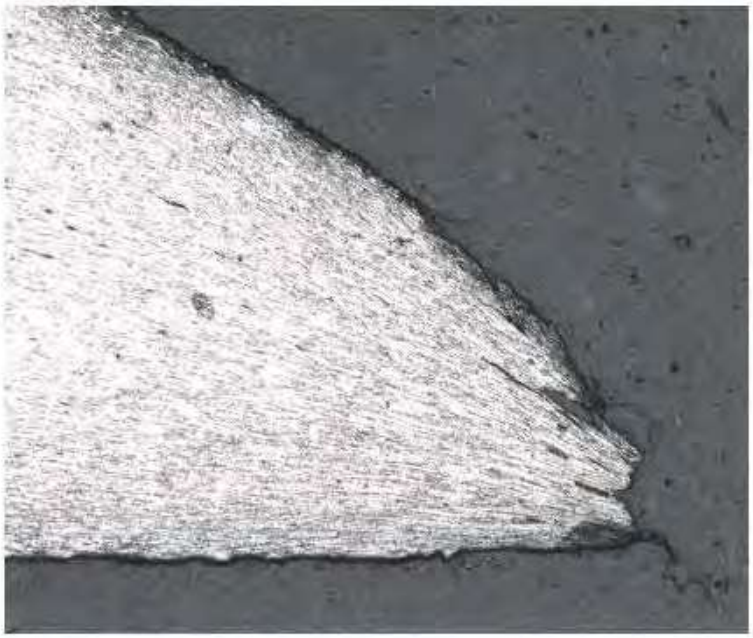


Figure 3-55-4—The fracture-edge microstructure displays severely elongated ferrite grains, proof of the ductility of the rupture. The thickness at the edge is about 0.01 in., which is a reduction in the wall thickness of more than 95 %. Magnification 50X, etched.

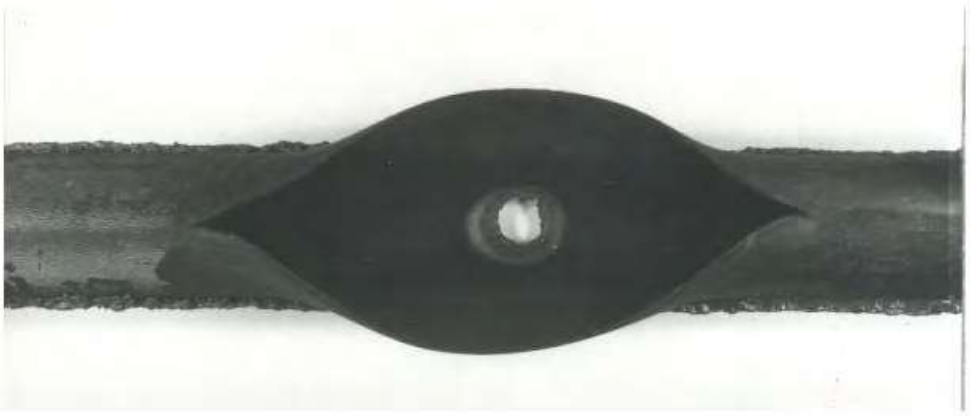


Figure 3-55-5—Short-term, high-temperature boiler tube failures from DNB are wide-open bursts with the failure lips drawn to a near knife edge. They are ductile ruptures. Magnification 25X.

3.56 Sigma Phase Embrittlement

3.56.1 Description of Damage

Formation of a metallurgical phase known as sigma phase in some stainless steels when they are heated above about 1000 °F (540 °C) can result in a loss of ductility and fracture toughness. The embrittlement can lead to cracking failure.

3.56.2 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) 400 series SS and other ferritic and martensitic stainless steel with > 17 % Cr are also susceptible (e.g. Types 430 and 440).

c) Duplex stainless steels.

3.56.3 Critical Factors

a) Alloy composition, temperature, and time at temperature are the critical factors.

    1. In susceptible alloys, the primary factor that affects sigma phase formation is the time of exposure at elevated temperature.

b) The metallurgical change is a precipitation of a hard, brittle intermetallic compound that can also render the material more susceptible to intergranular corrosion. The precipitation rate and amount increases with increasing chromium and molybdenum content.

c) Sigma phase forms 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 (540 °C to 925 °C). Embrittlement can result by holding within or cooling through the transformation temperature range.

d) Sigma forms most rapidly from the ferrite phase that exists in 300 series SS and duplex stainless steel weld deposits. It also readily forms in duplex stainless steel base metals due to their nominally 50 % ferrite phase. It can also form in 300 series SS base metal (austenite phase) but usually more slowly.

e) Some 300 series SS can exhibit about 10 % to 15 % sigma phase. Cast austenitic stainless steels, which typically have a high ferrite content (up to 40 %), can develop considerably more sigma than wrought austenitic stainless steels, and may have very poor high-temperature ductility.

f) Formation of sigma phase in austenitic stainless steel weld metals can occur in a few hours, as evidenced by the tendency for sigma to form in austenitic stainless steel weld overlay subjected to a PWHT at 1275 °F (690 °C) during the fabrication of heavy wall pressure vessels.

g) The tensile strength 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 operating stresses at operating temperatures but upon cooling 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 (540 °C).

    1. Tests performed on sigmatized 300 series SS (304H) samples from FCC regenerator internals have shown that even with 10 % sigma formation (a large amount), the Charpy impact toughness was still 39 ft-lb (53 J) at 1200 °F (650 °C).

2. 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 e.g. Figure 3-56-2.)

3.56.4 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 of the underlying Cr-Mo base metal.

c) Stainless steel heater tubes are susceptible and can be embrittled.

3.56.5 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 (Figure 3-56-3 to Figure 3-56-5) and impact testing (Table 3-56-1 and Table 3-56-2 and Figure 3-56-1).

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

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

3.56.6 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 temperature range.

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

c) 300 series SS can be de-sigmatized by solution annealing at 1950 °F (1065 °C) for 4 hr followed by a water quench. However, this is not practical for most equipment.

d) Sigma phase in welds is typically minimized by controlling the ferrite content, i.e. by specifying the allowable range of ferrite in the weld metal, e.g. in the range of 5 % to 9 % for Type 347 and somewhat less ferrite for Type 304. Limiting the maximum ferrite content minimizes sigma formation during service or fabrication. The minimum ferrite content is needed to minimize hot short cracking during welding.

e) For stainless steel weld overlayed Cr-Mo components, the fabrication plan and sequence should attempt to minimize the exposure of the overlay to base metal PWHT temperatures wherever possible, particularly in highly stressed locations.

3.56.7 Inspection and Monitoring

This damage mechanism is very difficult to find and is also time dependent. Thus, it may take a while to develop in service. Online inspection is not applicable. Awareness of susceptible equipment can help direct inspection planning.

a) Sigma phase formation and embrittlement can be detected by removing and lab testing a sample of the suspect material. Metallographic examination and/or impact testing can be used, as applicable.

b) For duplex stainless steels, ECT has been reported to find sigma phase embrittlement, primarily due to the change in microstructure. However, this is highly dependent upon the methodology employed as well as the knowledge and experience of the equipment operator.

c) FMR can be used to verify the presence of sigma phase in severe cases but normally will only assess the condition at the surface of the component, not the thru-wall extent of the damage.

3.56.8 Related Mechanisms

885 °F (475 °C) embrittlement (3.1).

3.56.9 References

1. API Recommended Practice 581, *Risk-Based Inspection Methodology,* American Petroleum Institute, Washington, DC.

2. *High Temperature Corrosion in Refinery and Petrochemical Service*, High Temperature Engineering Bulletin HTB-2, INCO, New York, NY, 1960.

3. L. Garverick, *Corrosion in the Petrochemical Industry*, ASM International, 1994, pp. 29 and 129–136.

4. R. Viswanathan, *Damage Mechanisms and Life Assessment of High-temperature Components*, ASM International, 1989.

5. *Metals Handbook—Desk Edition*, ASM International, Materials Park, OH.

6. J. Hau and A. Seijas, "Sigma Phase Embrittlement of Stainless Steel in FCC Service," Paper No. 06578, *Corrosion/2006*, NACE International, Houston, TX.

7. API Recommended Practice 577, *Welding Inspection and Metallurgy*, American Petroleum Institute, Washington, DC.

8. C.N. McCowan T.A. Siewert, and D.L. Olson, *Stainless Steel Weld Metal: Prediction of Ferrite Content*, WRC Bulletin 342, Welding Research Council, Shaker Heights, OH, 1989.

9. E.L. Creamer et al., "Embrittlement of Type 347 Stainless Steel Weldments by Sigma Phase," Welding Research Supplement, June 1969, pp. 239–244.

10. G. Psuj, T. Chady, and C.G. Camerini, "Eddy Current Transducer Dedicated for Sigma Phase Evaluation in Duplex Stainless Steel," *Journal of Sensors*, Vol. 2012, 2012.

11. K. Doughten, D. Bauer, M. Rakos, and P. Domenico, "Non-destructive Testing of Duplex Stainless Steel," *Stainless Steel World Americas Conference and Expo*, October 2012.

12. J. Hau, "Sigma Phase Embrittlement of Type 304H Stainless Steel After FCCU Service," Paper No. 09140, *Corrosion/2017*, NACE International, Houston, TX.

Table 3-56-1—Data for Property Trends of Toughness vs Temperature

Test Temperature	304 SS 2 % Sigma		321 SS 10 % Sigma		304 SS 1 % Sigma		304 SS 2 % Sigma		347 SS 1 % Sigma	
	% of Impact	% Shear	% of Impact	% Shear	% of Impact	% Shear	% of Impact	% Shear	% of Impact	% Shear
70 °F (21 °C)	21	0	7	0	—	—	21	10	30	90
500 °F (260 °C)	38	25	10	20	—	—	—	—	100	100
900 °F (480 °C)	44	50	15	40	20	10	—	—	100	100
1200 °F (650 °C)	63	100	21	60	71	90	77	90	100	100

NOTE 1 Percent of impact is a comparison to original impact strength of non-embrittled materials.

NOTE 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 3-56-2—Charpy V-notch (CVN) Impact Test Results, Absorbed Energy in Joules (ft-lb) from Reference 6

Refinery	Location	Years of Service	Sigma Phase Content (%)	Temperature	
				RT	Service
A	Base metal	17	4.0	85 (63)	145 (107)
A	Weld metal	17	8.7	37 (27)	100 (74)
B	Base metal	19	12.0	12 (9)	43 (32)
C	Base metal	13	1.5	35 (26)	75 (55)

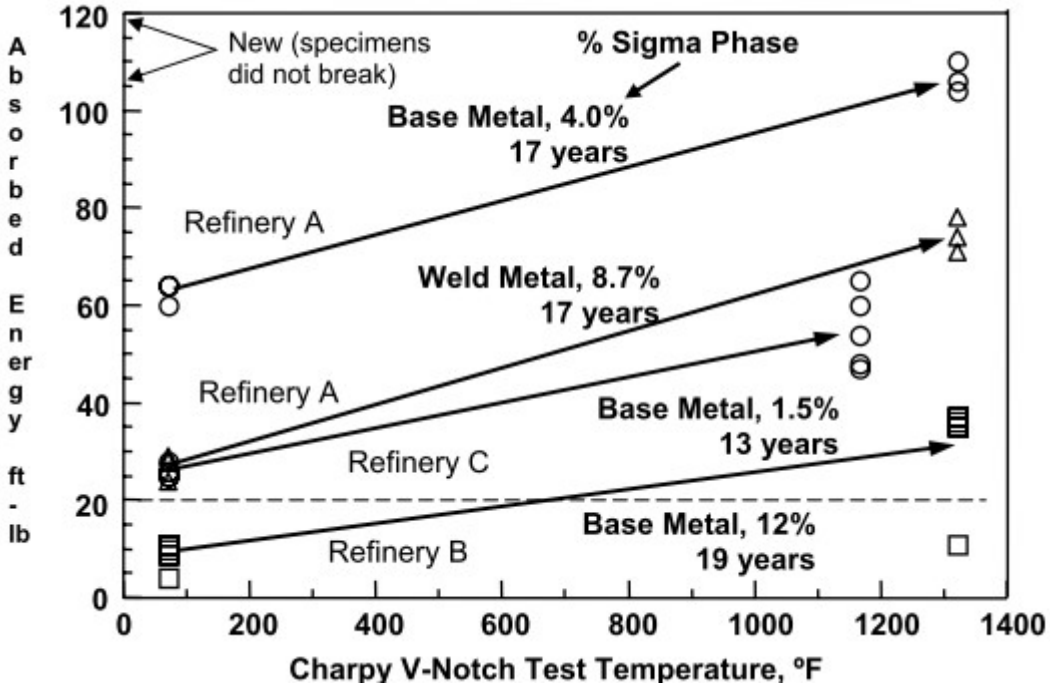
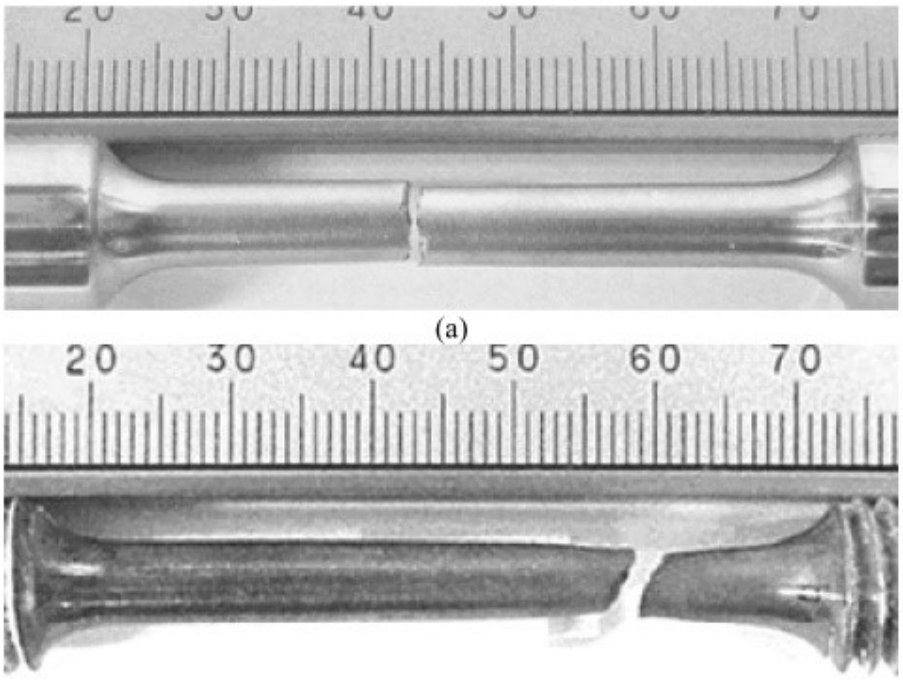


Figure 3-56-1—CVN impact test results as absorbed energy in ft-lb, at room temperature and service temperature. (Reference 6)



(a)

(b)

Figure 3-56-2—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 significant ductility and elongation at 1320 °F (716 °C). (Reference 6)

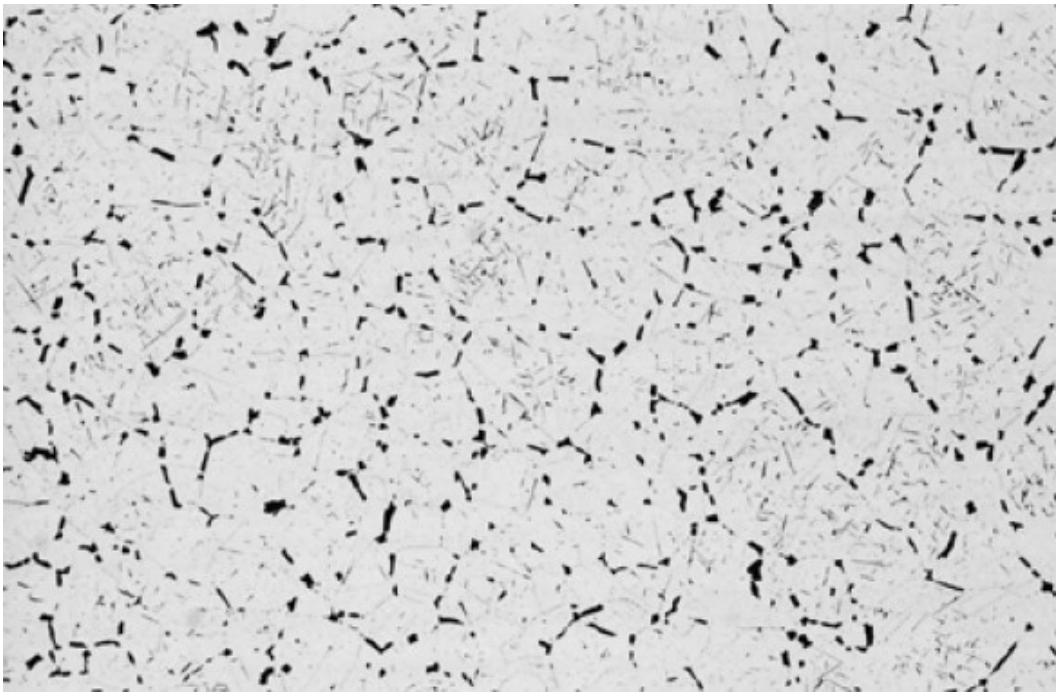


Figure 3-56-3—Microstructure of FCC regenerator plenum chamber wall, electrolytic etch in 33 % KOH, magnification 100X. Dark-etching particles are sigma phase; estimated amount is 6.0 %. (Reference 6)

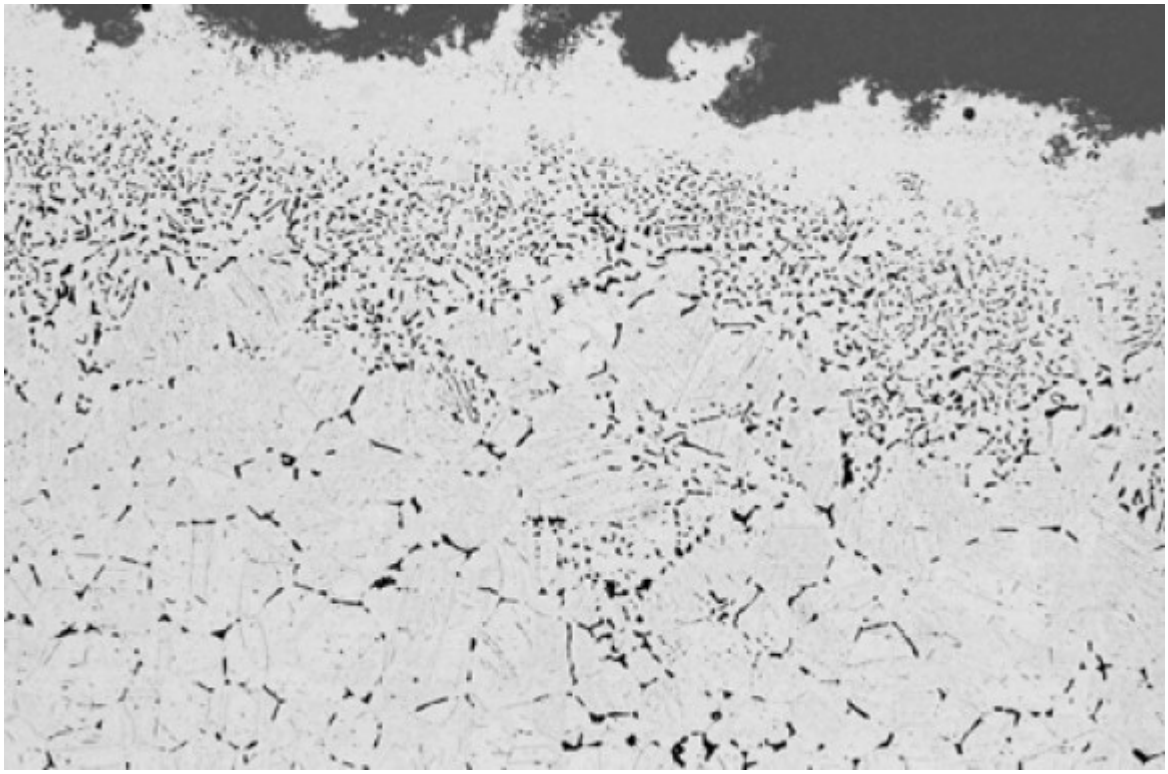
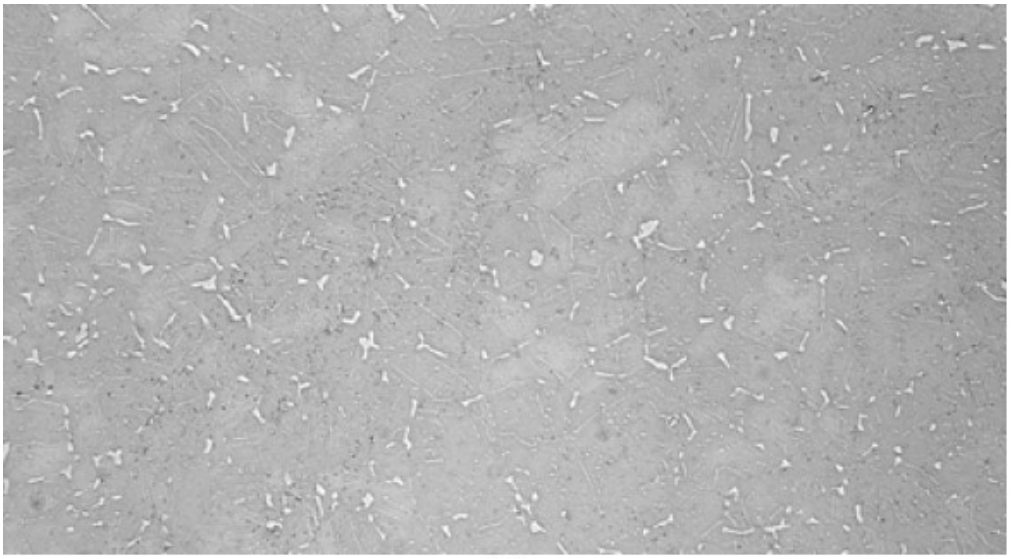
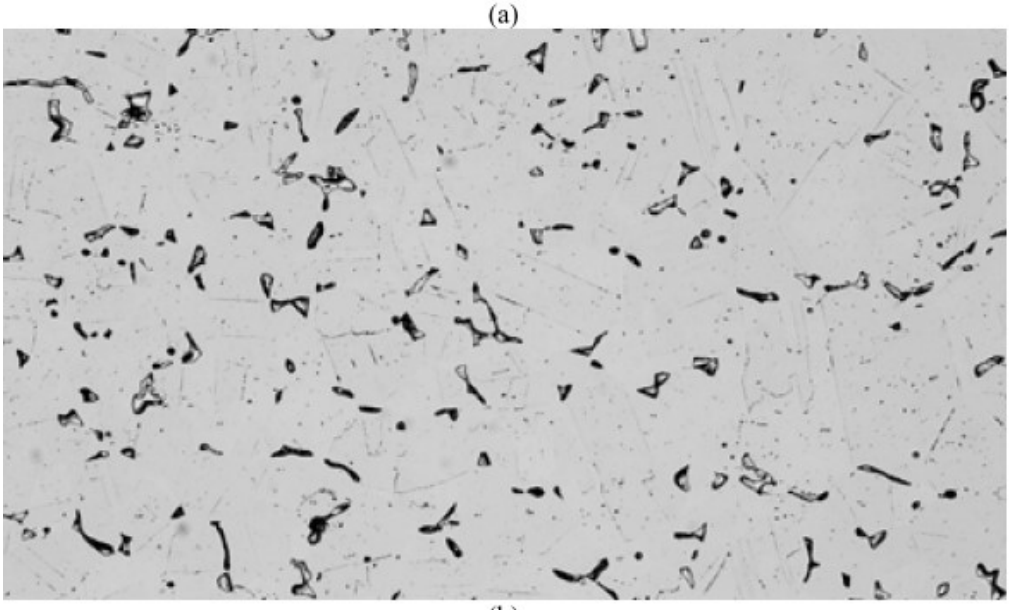


Figure 3-56-4—Dark-etching particles are sigma phase that are concentrated near the outside surface of FCC regenerator plenum chamber, electrolytic etch in 33 % KOH, magnification 100X. (Reference 6)



(a)



(b)

Figure 3-56-5—304H stainless steel with 14 years operation at a nominal temperature of 1320 °F (716 °C) after (a) etching in Vilella's reagent, magnification 100X, and (b) electrolytic etching in KOH, magnification 200X. The estimated amount of sigma phase was 5.0 %. (Reference 6)

3.57 Soil Corrosion

3.57.1 Description of Damage

The corrosion of metals from exposure to soils is referred to as soil corrosion.

3.57.2 Affected Materials

Carbon steel, cast iron, and ductile iron.

3.57.3 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 capability) and homogeneity (variation in soil type), cathodic protection, stray current drainage, and 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 580 and API 581.

c) Soil resistivity is related to the soil moisture content and dissolved electrolytes in the soil water. Soil resistivity testing is frequently used to estimate soil corrosivity, mainly because it is easy to measure; however, it can produce widely variable results within a single refinery site.

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 3-57-1)

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 MIC.

3.57.4 Affected Units or Equipment

a) Underground piping and equipment as well as buried tanks and the bottoms of aboveground storage tanks. (Figure 3-57-2)

b) Ground supported metal structures. (Figure 3-57-2)

c) Piping running close to the ground under which soil has accumulated over the years to the point of reaching and contacting or partially covering the pipe.

d) Piping exiting road or other crossings where soil has sloughed off and is laying on or covering the pipe.

3.57.5 Appearance or Morphology of Damage

a) Soil corrosion appears as external thinning with a roughened surface and localized deeper attack or pitting.

b) Poor condition of a protective coating is a tell-tale sign of potential corrosion damage.

c) Soil corrosion can be highly variable along an unprotected buried pipe or on the unprotected underside of a storage tank bottom. (Figure 3-57-3)

3.57.6 Prevention/Mitigation

Soil corrosion of carbon steel can be minimized through the use of appropriate coatings and cathodic protection along with special backfill to prevent rock damage to the coating. The most effective protection is a combination of a corrosion-resistant coating and a cathodic protection system.

3.57.7 Inspection and Monitoring

The following techniques can be used for inspecting buried or on-grade metallic components that may have become covered by shifting soil, as well as soil-to-air interfaces.

a) An aboveground visual survey can identify leaks coming to the surface of the soil.

   NOTE Any change in the surface contour of the ground, discoloration of the soil, softening of paving asphalt, pool formation, bubbling water puddles, or noticeable odor.

b) Smart-pigging devices employing UT or MFL can be used where the piping is designed to send and receive the pigs or accommodate tethered pigs that can be sent through lines. It can detect dents, flaws, and corrosion.

c) A close-interval potential survey on a cathodically protected line may be used to verify that the buried piping has a protective potential throughout its length. API 570 provides guidance for conducting close-interval surveys. Close-interval potential surveys can only infer wall loss from CP potential, but not directly detect presence of wall loss, and thus they identify areas for follow-up inspection. Refer to NACE SP0169 and API 651 Section 11 of for guidance applicable to inspecting and maintaining cathodic protection systems for buried and soil-contacting equipment.

d) A pipe coating holiday survey (e.g. direct current voltage gradient) can be used to locate coating defects on coated pipes. This can be performed on newly coated pipe before being buried or on pipe that has been excavated.

e) VT of the pipe or equipment coating after excavation is one of the most reliable methods to determine its condition. This is also commonly done at the soil-to-air interface, where the soil should be removed down to about 12 in. (305 mm) below the surface to expose the most corrosion-prone area. Care should be taken during excavation to avoid damaging the coating or the equipment. Risks of excavating pipe while in service should be evaluated.

f) GWT can provide a screening tool for metal loss on buried piping, but signal loss can limit the distance from the GWT collar over which the piping can be inspected.

g) Pressure testing can determine whether buried equipment is leaking at that particular time but does not provide information concerning the degree of corrosion on the equipment.

3.57.8 Related Mechanisms

Galvanic corrosion (3.31), concentration cell corrosion (3.19), graphitic corrosion (3.33), and MIC (3.45).

3.57.9 References

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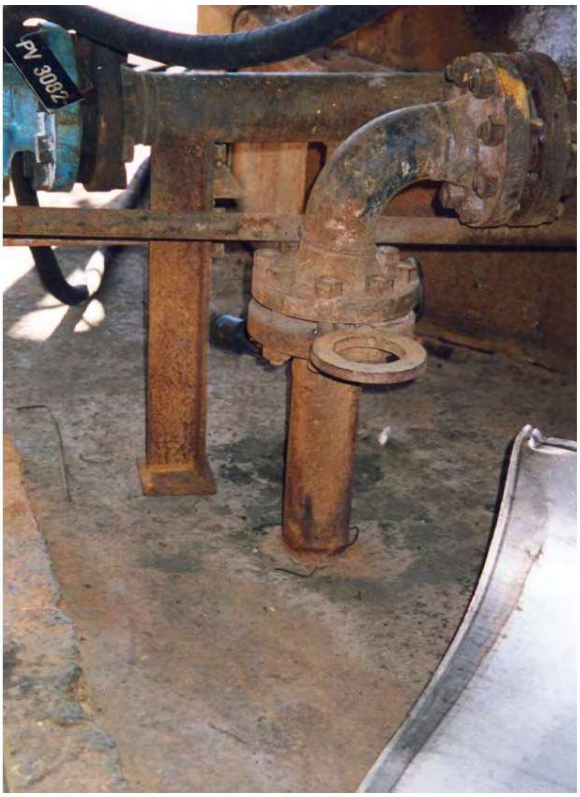

Figure 3-57-1—Corrosion of carbon steel pipe at the soil/air interface where the pipe emerges from underground.

Figure 3-57-2—Coupons removed from the bottom of an unprotected steel condensate storage tank after 3 years of service. The external surface is shown.

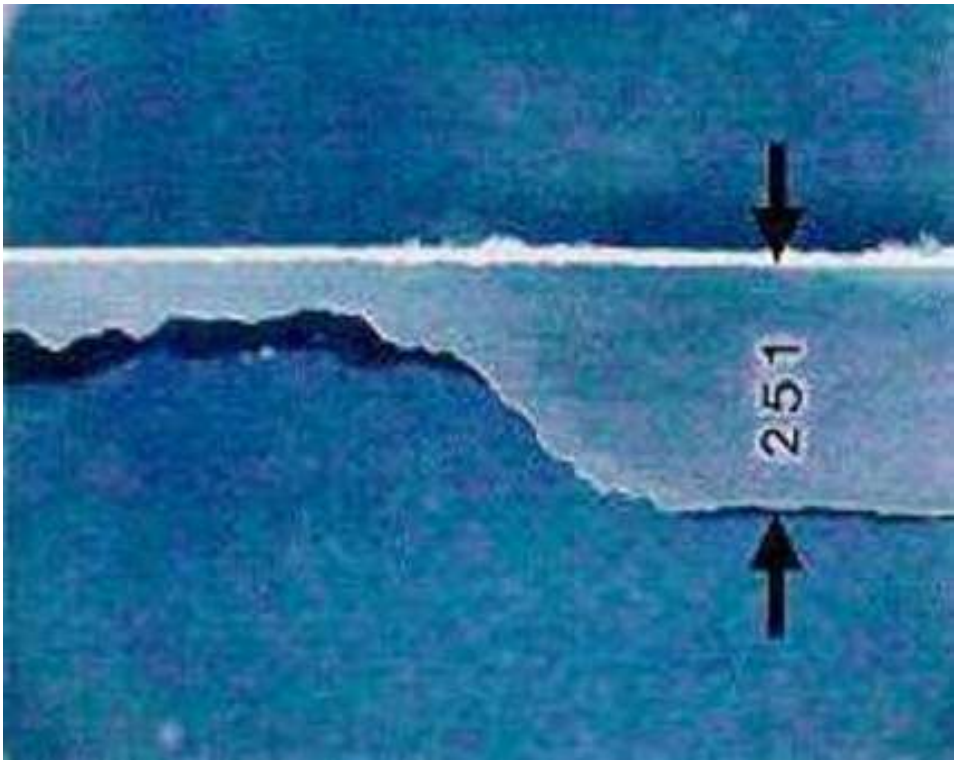

Figure 3-57-3—Cross section through location (A) showing severe corrosion. The arrows point to a location that was at the original thickness.

3.58 Sour Water Corrosion (Acidic)

3.58.1 Description of Damage

a) Corrosion of steel (primarily) due to acidic sour water (SW) containing H_2S at a pH between 4.5 and 7.0. Carbon dioxide (CO_2) may also be present as well as other acidic species such as dissolved organic acids.

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

3.58.2 Affected Materials

a) Primarily affects carbon steel.

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

3.58.3 Critical Factors

a) H_2S content, pH, temperature, velocity, and oxygen concentration are all critical factors.

b) The H_2S concentration in the SW is dependent on the H_2S partial pressure in the gas phase as well as temperature and pH.

c) At a given pressure, the H_2S concentration in the SW decreases as temperature increases.

d) Increasing concentrations of H_2S tend to decrease solution pH down to about 4.5. Streams with a pH below 4.5 indicate the presence of a strong acid, which would be the main corrosion concern.

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

f) In some instances, at a pH above 4.5, a thicker, porous sulfide film layer can form. This can promote pitting under the sulfide deposits.

g) Other contaminants have a significant effect on water pH. For example, HCl and CO_2 reduce the pH (make it more acidic). Ammonia significantly increases pH and is more often associated with alkaline SW where the main concern is ammonium bisulfide corrosion. (See 3.5.)

h) The presence of air or oxidants may increase the corrosion rate and usually produces pitting or under-deposit attack.

3.58.4 Affected Units or Equipment

Acidic SW corrosion is a concern in overhead systems of FCC and coker gas fractionation plants with high H_2S levels and low NH_3 levels.

3.58.5 Appearance or Morphology of Damage

a) Corrosion damage from acidic SW is typically general thinning. However, localized corrosion or localized under-deposit attack can occur, especially if air or oxygen is present. (Corrosion in high-CO_2 environments caused primarily by the CO_2 is covered in 3.18.)

b) 300 series SS is susceptible to pitting attack and may experience crevice corrosion and/or Cl^- SCC. (See 3.17.)

3.58.6 Prevention/Mitigation

a) Process monitoring and control are important for minimizing the effects of acidic SW corrosion. Process parameters that typically should be monitored, e.g. at water draws of overhead accumulators, and controlled where applicable, are as follows:

1. H_2S content,
2. pH,
3. chloride content,
4. cyanide content,
5. temperature,
6. fluid velocity, and
7. oxygen concentration.

b) 300 series SS can be used at temperatures below about 140 °F (60 °C) where Cl^- SCC is not likely.

c) Copper alloys and nickel alloys are generally not susceptible to acid SW corrosion. However, copper alloys are vulnerable to corrosion and some are susceptible to SCC in environments with ammonia.

d) Water wash injection into FCC overheads and coker light ends units dissolves and dilutes corrodents like H_2S and cyanide (CN^-). Additional injection of a polysulfide solution with the water wash helps to convert cyanides into a less harmful compound.

3.58.7 Inspection and Monitoring

a) UT scanning and RT can identify locally thinned areas of equipment exposed to SW corrosion.

b) Permanently mounted thickness monitoring sensors can be used.

c) Strategically placing continuous corrosion monitoring in the system, e.g. corrosion probes, corrosion coupons, or online thickness monitoring sensors, can provide an early indication of increased corrosion rates and the need to conduct thickness surveys or apply more advanced NDE to verify the severity and extent of the indicated corrosion.

NOTE Corrosion probes may provide misleading data due to formation of FeS scale on the probe.

d) Process monitoring and control, as described in 3.58.6 above, are key to controlling acidic SW corrosion and helping identify areas that should be included in the inspection plan.

3.58.8 Related Mechanisms

Other damage mechanisms to consider in these environments include wet H_2S damage (3.67) and CO_2 corrosion (3.18). See also ammonium bisulfide corrosion (3.5) and concentration cell corrosion (3.19).

3.58.9 References

1. J. Gutzeit, “Corrosion of Steel by Sulfides and Cyanides in Refinery Condensate Water,” *Materials Protection*, December 1968, pp. 17–23.

2. R.H. Hausler and N.D. Coble, “Corrosion Control in Crude Unit Overhead Systems,” Paper 42-72, *API 37th Midyear Meeting*, May 1972.

3. B.D. Craig, “The Nature of Sulfides Formed on Steel in an H_2S-O_2 Environment,” *CORROSION*, Vol. 35, No. 3, March 1979, p. 136–138.

4. C.P. Dillon, *Corrosion Control in the Chemical Process Industries*, Materials Technology Institute (printed by NACE), MTI Publication No 45, Second Edition, St. Louis, MO, 1994.

5. D.A. Jones, *Principles and Prevention of Corrosion*, Prentice-Hall, New York, NY, 1996.

6. B.D. Craig, “Sour-gas Design Considerations,” *Society of Petroleum Engineers (SPE) Monograph Series*, Monograph Volume 15, 1993.

3.59 Spheroidization (Softening)

3.59.1 Description of Damage

Spheroidization is a change in the microstructure of steels resulting from exposure in the 850 °F to 1400 °F (440 °C to 760 °C) range, where the carbide phases in carbon steels and C-½Mo steels are unstable and may agglomerate from their normal plate-like form to a spheroidal form or from small, finely dispersed carbides in Cr-Mo steels to large agglomerated carbides. Spheroidization may cause a loss in strength and/or creep resistance.

3.59.2 Affected Materials

All commonly used grades of carbon steel and low-alloy steels including C-½Mo, 1Cr-½Mo, 1¼Cr-½Mo, 2¼Cr-1Mo, 3Cr-1Mo, 5Cr-½Mo, and 9Cr-1Mo steels.

3.59.3 Critical Factors

a) Metal chemical composition, 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 (550 °C) but may take several years at 850 °F (455 °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.

3.59.4 Affected Units or Equipment

a) Spheroidization can occur in piping and equipment after exposure to temperatures above 850 °F (455 °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 boiler tubes and fired heater tubes in process units may be affected by a loss in creep strength, but equipment is seldom renewed or repaired because of spheroidization.

3.59.5 Appearance or Morphology of Damage

a) Spheroidization is not visible or readily apparent and can only be observed through metallography. In carbon steel, the pearlite phase undergoes a time-dependent transformation from partial to complete spheroidization. (Figure 3-59-1 and Figure 3-59-2)

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

3.59.6 Prevention/Mitigation

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

3.59.7 Inspection and Monitoring

a) Spheroidization is primarily found using FMR or removal of samples for metallographic evaluation.

b) Because spheroidization may result in a reduction in tensile strength (and therefore, hardness), field hardness testing may indicate the presence of spheroidization, but it should be followed up with sampling and/or FMR to confirm its existence.

3.59.8 Related Mechanisms

Closely related to graphitization (3.34). Spheroidization and graphitization are competing mechanisms that occur at overlapping temperature ranges. At temperatures above about 1025 °F (550 °C), graphitization may occur after spheroidization. Below 1025 °F (550 °C), graphitization occurs before the steel is fully spheroidized.

3.59.9 References

1. *ASM Handbook—Properties and Selection: Iron, Steels, and High-performance Alloys*, Volume 1, ASM International, Materials Park, OH.

2. D.N. French, “Microstructural Degradation,” The National Board of Boiler and Pressure Vessel Inspectors, http://www.nationalboard.com, June 2001.

3. R.D. Port, “Non-weld-related Graphitization Failures," Paper No. 248, *Corrosion/89*, NACE International, Houston, TX.

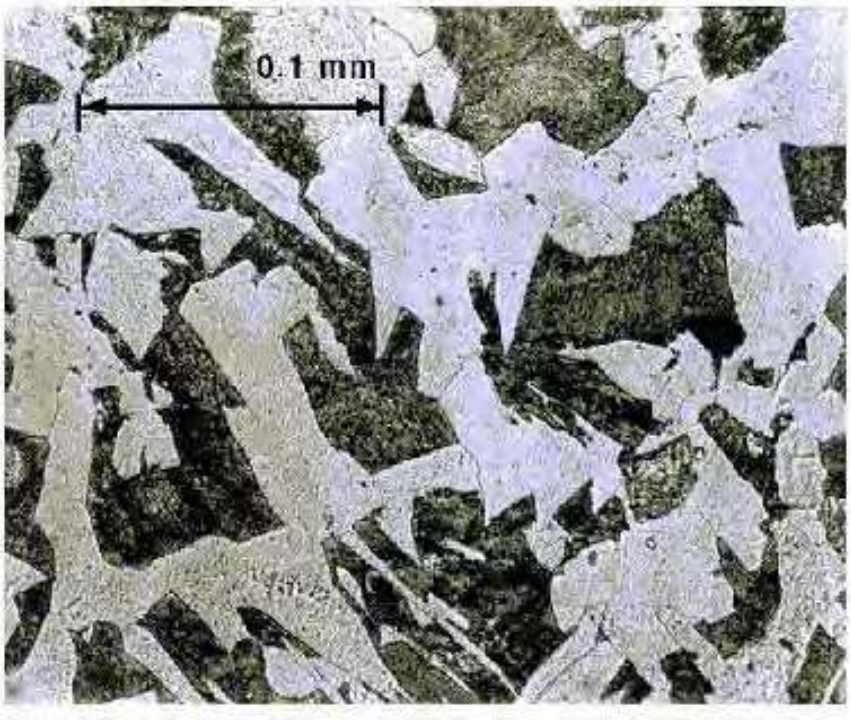

Figure 3-59-1—High-magnification photomicrograph of metallographic sample showing typical ferrite-pearlite structure of carbon steel.

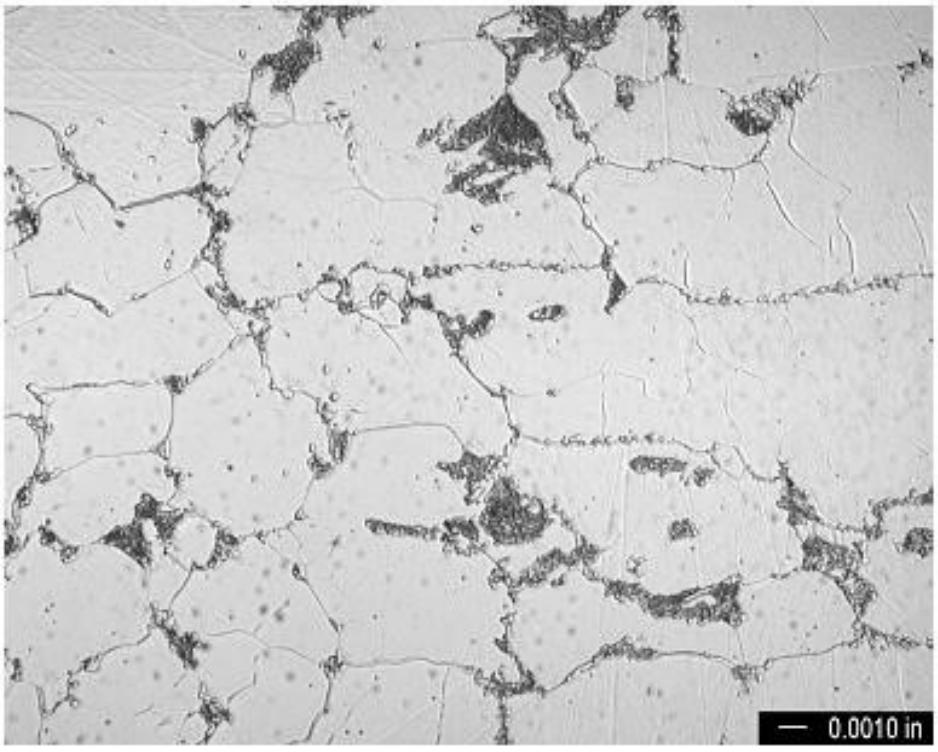

Figure 3-59-2—High-magnification photomicrograph of metallographic sample showing spheroidized carbides.

3.60 Strain Aging

3.60.1 Description of Damage

Strain aging is a form of metallurgical damage found mostly in older (pre-1980) carbon steels and C-½Mo low-alloy steels that were not fully deoxidized as more modern steels are. It is associated with older steel-making processes such as the Bessemer and open hearth processes, which use air instead of oxygen to remove carbon. Strain aging occurs in a susceptible steel 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. Strain aging is a concern because it increases the chances of brittle fracture.

3.60.2 Affected Materials

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

3.60.3 Critical Factors

a) Steel composition and manufacturing process determine steel susceptibility.

b) Steels manufactured by the Bessemer or open hearth process, both of which use air to remove carbon, contain a higher level of nitrogen than newer steels manufactured by the basic oxygen furnace process.

c) In general, steels made by the basic oxygen furnace process and fully killed (deoxidized) with aluminum will not be susceptible. The effect is found in steels with higher levels of nitrogen and carbon, but not in the modern fully deoxidized carbon steels.

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, typically following repair welds that were not PWHT'd.

f) The pressurization sequence vs temperature is a critical issue to prevent brittle fracture of susceptible equipment.

g) Strain aging can also occur when welding susceptible materials, especially in areas near stress concentrations, at closely spaced welds, or in repairs. When strain aging occurs during the welding cycle as a result of the combined effects of the heat of welding and residual welding stresses, it has been termed dynamic strain aging.

3.60.4 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.

3.60.5 Appearance or Morphology of Damage

Strain aging can be revealed through detailed metallurgical analyses, but damage most likely will not be identified as strain aging until fracture has already occurred. In cases where strain aging results from metal forming at ambient temperature and then aging at an intermediate temperature in service, the effects of stain aging have been observed by an increase in the hardness.

3.60.6 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 *BPVC* Section VIII, Division 1 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, because heating in the temperature range of 1100 °F to 1200 °F (595 °C to 650 °C) eliminates the strain that causes the embrittlement. Where PWHT is not possible, buttering should be considered to minimize welding residual stresses acting on the old material being welded.

3.60.7 Inspection and Monitoring

a) There are no commercially available online inspection or monitoring techniques to detect strain aging.

b) Hardness testing can be used in cases where strain aging has occurred over a large area of the material. Hardness testing is not effective in detecting strain aging embrittlement resulting from welding.

3.60.8 Related Mechanisms

When deformation occurs at the intermediate temperature, as is the case of welding, the mechanism is referred to as dynamic strain aging. Blue brittleness is another form of strain aging.

3.60.9 References

1. ASME *Boiler and Pressure Vessel Code*, Section VIII, Division 1, American Society of Mechanical Engineers, New York, NY.

3.61 Sulfidation

3.61.1 Description of Damage

Corrosion of carbon steel and other alloys resulting from their reaction with sulfur compounds in high-temperature environments. Corrosion in the presence of hydrogen is discussed in 3.35, *High-temperature H_2/H_2S Corrosion*. In this discussion, sulfidation will refer to high-temperature sulfidic environments without hydrogen. This mechanism is also known as sulfidic corrosion. Because of the smooth, large, relatively uniformly corroded surface produced by sulfidation, it can lead to rupture type failure rather than a localized or pinhole leak. Both types of sulfidation, with and without hydrogen present, are covered in much more detail in Reference 6 (API 939-C).

3.61.2 Affected Materials

a) All iron-based materials including carbon steel and low-alloy steels, 400 series SS, and 300 series SS, in that order from most susceptible to less susceptible.

b) Nickel-based alloys are also affected to varying degrees depending on composition, especially chromium content. Above 1193 °F (645 °C), alloys containing high nickel contents can suffer a form of sulfidation and metal loss associated with the formation of nickel sulfides beneath the metal surface. This has also been referred to as hot corrosion. Susceptibility to this form of sulfidation increases with increasing nickel content.

c) Copper-based alloys form sulfide corrosion product at lower temperatures than carbon steel.

3.61.3 Critical Factors

a) Major factors affecting sulfidation are chemical composition of the metal, temperature, and concentration of corrosive (reactive) sulfur compounds. Flow conditions can also affect the rate of damage.

b) In general, the resistance of iron-based and nickel-based 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 high-temperature sulfidation process environments. Nickel-based alloys are similar to stainless steels in that similar levels of chromium provide similar resistance to sulfidation; however, nickel alloys with little or no chromium can have poor resistance to these environments.

c) Figure 3-61-1 and Figure 3-61-2 show the typical effects of increasing chromium content, temperature, and sulfur content on metal loss. These curves only indicate the general trends in the effects of chemical composition, temperature, and sulfur content on corrosion rates. They are used in design for estimating the corrosion rate for a particular service but should be regarded as only showing trends, as actual observed rates can often vary substantially. In many cases the predictions are conservative, i.e. they overstate the actual corrosion rates found in service. The references at the end of this section provide additional background on the development of these curves.

d) The silicon content of carbon steel can significantly affect its susceptibility to sulfidation. Carbon steels with Si content less than 0.10 % have been found to suffer variable and often higher sulfidation corrosion rates than carbon steel with silicon content above this level. (Higher-Si carbon steels are still susceptible to sulfidation, but steel with low Si content may suffer higher rates.) Silicon-killed steel has greater than 0.10 % Si, while non-killed steels generally do not. There have been a number of incidents in the refining industry where lower-Si ASTM Grade A53 piping suffered significantly more metal loss than ASTM Grade A106 piping or standard carbon steel pipe fittings or flanges welded to the A53 pipe.

e) The amount of metal loss suffered in a particular service is greatly affected by the material's ability to form a protective sulfide scale. While sulfide scale invariably forms as a corrosion product on the metal surface, the degree to which it is protective depends on its thickness, density, adherence, and completeness of coverage, which depend on its chemical composition and the severity of the process stream, including flow regime.

f) Sulfidation (H_2-free) of iron-based alloys begins at metal temperatures above 450 °F (230 °C) but normally only becomes a practical concern above 500 °F (260 °C). Experience has shown 500 °F (260 °C) to be the most useful service temperature above which to focus inspection, monitoring, and corrosion mitigation efforts.

g) Crude oils and other hydrocarbon streams contain sulfur compounds at various concentrations. Total sulfur content is made up of many different sulfur or sulfide species.

h) Sulfidation is primarily caused by H_2S and other reactive sulfide species formed by 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 of sulfur alone. Knowing the total "reactive sulfur" in the process stream is key to predicting or assessing its actual corrosivity.

3.61.4 Affected Units or Equipment

a) Sulfidation occurs in piping and equipment in high-temperature environments where sulfur-containing liquid, vapor, or mixed streams are processed.

b) Crude, vacuum, FCC, coker, and visbreaker units, as well as the feed sections of hydroprocessing units upstream of hydrogen injection [at which point high-temperature H_2/H_2S corrosion (3.35) begins to govern], commonly process these high-temperature, sulfur-containing streams without, or prior to, intentionally added hydrogen.

c) Coker heaters fabricated from higher-nickel alloys such as Alloy 800H have shown accelerated sulfidation corrosion rates in the lower radiant sections operating with tube metal temperatures exceeding 1193 °F (645 °C) as compared to similar tubes operating below this temperature.

d) Heaters fired with oil, gas, coke, and most other sources of fuel may be affected depending on sulfur levels in the fuel; it is now uncommon for heaters to be fired with anything but gas, usually low-sulfur gas to meet environmental restrictions, especially in the United States.

3.61.5 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 3-61-3 to Figure 3-61-7)

b) While generally having a uniform thinning morphology, the amount of thinning can vary at different locations in the system or at different locations along the length of a piping run.

1. The difference in the degree of thinning between low-Si (<0.10 % Si) pipe and higher-Si (≥0.10 Si) pipe in the same system can be large, with a marked step change in remaining wall thickness at the transition. See Figure 3-61-4 and Figure 3-61-5.

c) A sulfide scale will usually cover the surface of components. Deposits may be thick or thin depending on the alloy, corrosiveness of the stream, and fluid flow regime and velocity.

3.61.6 Prevention/Mitigation

a) Resistance to sulfidation is generally achieved by upgrading to a higher-chromium steel such as 9Cr-1Mo.

b) Piping and equipment constructed from solid or clad (or overlaid) 300 series SS should provide significant resistance to corrosion. 400 series SS cladding should also provide significant improvement over carbon steel. Solid 400 series SS is generally not selected for piping or other pressure-containing equipment because of embrittlement and fracture toughness concerns.

c) Aluminum diffusion treatment of carbon steel and low-alloy steel components is sometimes used to reduce sulfidation rates and minimize scale formation; however, it may not offer complete protection.

d) For operation above 1193 °F (645 °C), sulfidation rates of higher-nickel alloys can be reduced by selecting an alloy with a lower Ni content.

3.61.7 Inspection and Monitoring

a) Thinning in piping, tubing, and other equipment can be detected and measured using UT thickness measurement or RT. Thinning in pressure vessels and large-diameter piping where internal inspection is possible can be detected by internal VT, typically followed up with UT.

b) Permanently mounted thickness monitoring sensors can be used.

c) Thinning in heater tubes can be detected using UT or by smart pigging. Smart pigging provides significantly more coverage than spot UT and may find thinning missed by spot UT.

d) Actual operating temperatures should be verified and compared against design. Temperatures and sulfur levels should be monitored for increases above design.

e) Temperatures can be monitored using tube-skin thermocouples and/or infrared thermography.

f) Proactive and retroactive MVPs (materials verification programs) can be used for alloy verification and to check for alloy mix-ups in services where sulfidation is anticipated. (API 578 provides guidance on MVPs.) See Figure 3-61-6.

g) Most refiners have instituted programs to identify low-Si carbon steel piping or components in sulfidation service by measuring the thickness of components in vulnerable piping systems. A small number of refiners have followed a PMI-type approach to measuring or otherwise determining the Si content of piping components.

3.61.8 Related Mechanisms

Sulfidation is also known as sulfidic corrosion. High-temperature sulfidation in the presence of hydrogen is covered in 3.35.

3.61.9 References

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

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. J. Gutzeit, R.D. Merrick, and L.R. Scharfstein, “Corrosion in Petroleum Refining and Petrochemical Operations,” *Metals Handbook*, Volume 13, ASM International, Materials Park, OH, 1987, pp. 1262–1287.

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.

6. API Recommended Practice 939-C, *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries*, American Petroleum Institute, Washington, DC.

7. API Recommended Practice 578, *Guidelines for a Material Verification Program (MVP) for New and Existing Assets*, American Petroleum Institute, Washington, DC.

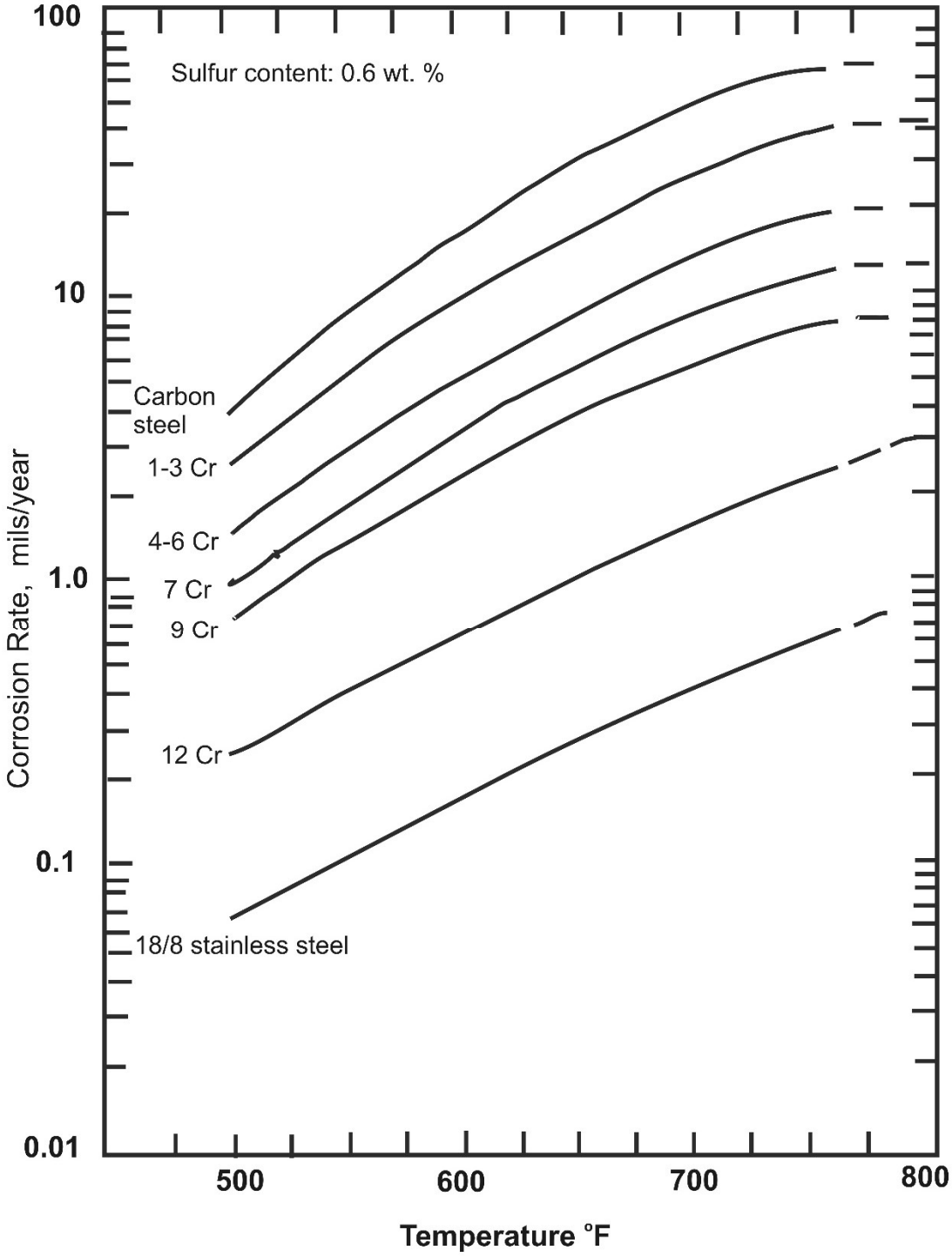

Figure 3-61-1—Modified McConomy curves showing typical effect of temperature on high-temperature sulfidation of steels and stainless steels. (Reference 3)

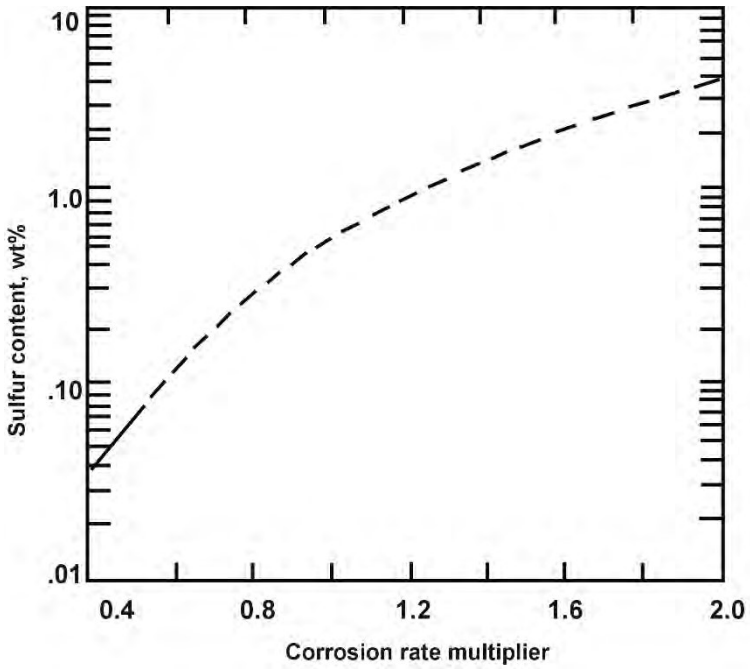

Figure 3-61-2—Multiplier for corrosion rates in Figure 3-61-1 based on the sulfur content of process fluid. (Reference 3)

Figure 3-61-3—Sulfidation failure of an 8-in. carbon steel pipe. Note the relatively uniform thinning that resulted in a sizeable rupture.

Figure 3-61-4—Sulfidation failure illustrating the effect of accelerated corrosion due to low silicon content. This 8-in. pipe section in FCC bottoms piping was in service at 150 psig (1 Mpa) at 650 °F to 700 °F (340 °C to 370 °C). The piping sketch in Figure 3-61-5 illustrates the difference in corrosion rate as compared to adjacent high-silicon components.

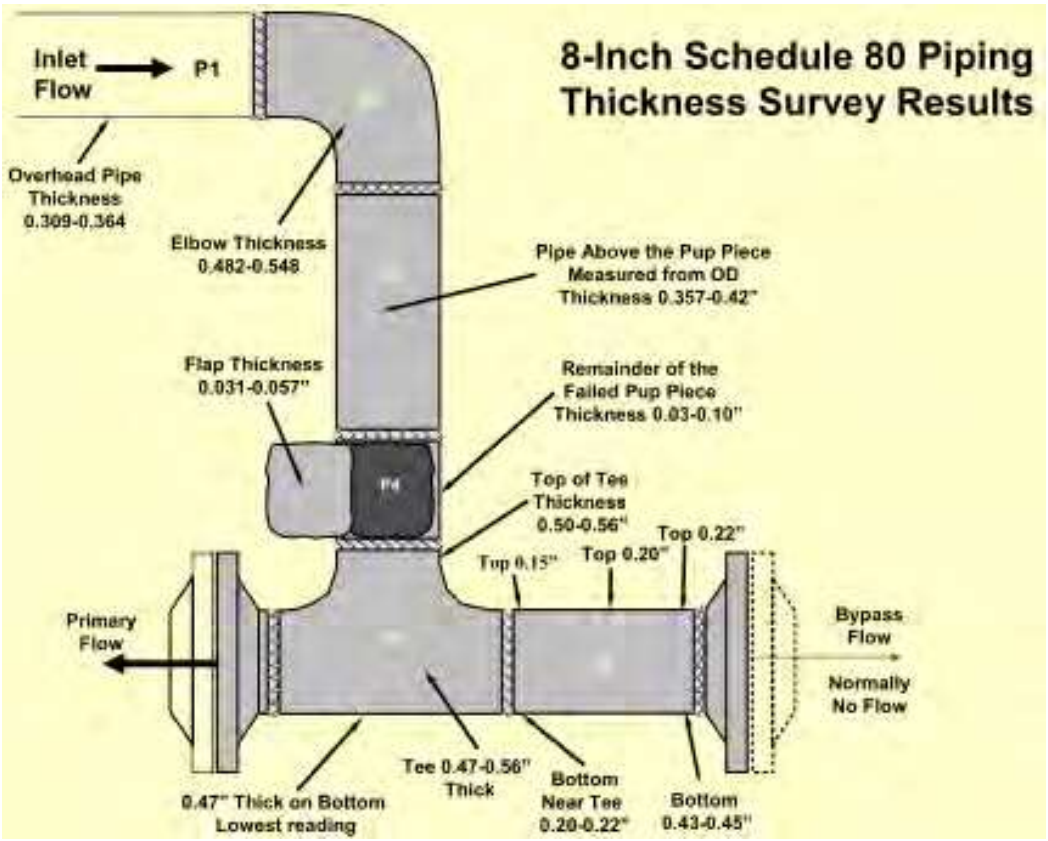

Figure 3-61-5—Thickness survey of 8-in. pipe shown in Figure 3-61-4 above.

Figure 3-61-6—Sulfidation failure of a carbon steel sight glass nipple on the right after 2 years in a crude unit. Original thickness is shown on left for comparison. Material was supposed to be 9Cr-1Mo.

Figure 3-61-7—Sulfidation failure of piping elbow.

3.62 Sulfuric Acid Corrosion

3.62.1 Description of Damage

Sulfuric acid promotes general and localized corrosion of carbon steel and other alloys. Carbon steel HAZs may experience accelerated corrosion.

3.62.2 Affected Materials

In order of increasing resistance: carbon steel, 316L SS, Alloy 20, high-silicon cast iron, high-nickel cast iron, Alloy B-2, and Alloy C-276.

3.62.3 Critical Factors

a) Acid concentration, temperature, alloy content, velocity, contamination, and presence of oxidizers.

b) Figure 3-62-1 shows a plot of carbon steel corrosion rates as a function of sulfuric acid concentration and temperature.

c) Corrosion of steel by dilute acid is usually in the form of overall metal loss or pitting and becomes more severe with increasing temperature and velocity.

d) Carbon steel corrosion rates increase significantly if the flow velocity exceeds about 2 fps to 3 fps (0.6 m/s to 0.9 m/s) or at acid concentrations below 65 %, since these conditions reduce the ability to maintain a protective ferrous sulfate scale.

e) Under stagnant or low-flow conditions [<0.5 fps (<0.15 m/s)], a mechanism known as hydrogen grooving can occur where movement of hydrogen bubbles on the steel surface removes the protective film and locally increases the corrosion rate. It is essentially an erosion-corrosion mechanism. Hydrogen grooving can cause corrosion along the sides and top of piping and equipment.

f) Mix points where acid is mixed with neutral or alkaline water cause heat to be released, with the resulting elevated temperature causing an acceleration of the corrosion rate. High corrosion rates can also occur where concentrated acid becomes diluted.

g) The presence of oxidizers (e.g. oxygen) or contaminants (e.g. iron) can greatly increase the corrosion rate, especially for Alloy B-2.

h) Stainless steel performance can be similar to carbon steel, especially in <92 % H_2SO_4 or at elevated temperatures. The addition of Mo to 300 series SS can improve corrosion resistance in <92 % H_2SO_4, but performance is still unpredictable due to the ability of the acid to act as either a reducing acid or an oxidizing acid depending on concentration and contaminants.

3.62.4 Affected Units or Equipment

a) Sulfuric acid alkylation units and waste water treatment plants are affected.

b) Areas of vulnerability in sulfuric acid alkylation units include contactors, reactor effluent lines, reboilers, deisobutanizer overhead systems, and the caustic treating section. (Figure 3-62-2 and Figure 3-62-3)

c) Acid and acid esters can carry over from the treating section and get into the distillation section. Acid concentrates in the reboilers and boils into the overhead. Similarly, acid esters can thermally decompose in the distillation section reboilers to form sulfurous or sulfuric acid, both of which vaporize and travel to the overhead.

d) Rivulet corrosion can occur in tanks and vessels where dilute acid refluxes down the sides of the tank or vessel. This condition can also occur at the air to liquid interface or rag layer.

e) Hydrogen grooving can occur in low-flow or stagnant areas such as in storage tanks, rail cars, or dead-legs.

f) Vessels handling sulfuric acid can be severely corroded when cleaning the vessel for internal inspection. Mixing concentrated sulfuric acid with cleaning water (which will also release a lot of heat and energy) will form dilute, highly corrosive acid that can cause a lot of damage in short period of time.

3.62.5 Appearance or Morphology of Damage

a) Attack can be localized or general depending upon acid concentration, flow velocity, and the location of vapor/liquid interface areas.

1. Localized corrosion can occur in piping or other areas with high flow.

2. Carbon steel weld HAZs can be attacked rapidly.

3. Rivulet corrosion, hydrogen grooving, and corrosion at the vapor/liquid or air/liquid interface are localized.

b) Localized corrosion can be so uniform that VT may not notice the transition from shallow to deep metal loss.

c) “Knife-line” grooving is typical at tops of horizontal piping where hydrogen bubbles form and travel along the top of the pipe. Areas of “fan”-shaped or “delta”-shaped corrosion are common at elbows.

d) Sulfuric acid attacks slag left from welding.

e) If the corrosion rate and velocity are high, there will be no scale.

3.62.6 Prevention/Mitigation

a) Corrosion is minimized through proper materials selection and proper operation within design velocities.

b) Alloys such as Alloy 20, Alloy 904L, and Alloy C-276 resist dilute acid corrosion and form a protective iron sulfate film on the surface.

c) Acidified product streams can be washed with caustic to neutralize the acid.

d) Because the cleaning of vessels containing concentrated H_2SO_4 can cause serious corrosion [see 3.62.4 f)], when carbon steel (or other non-resistant material) vessels must be emptied, a neutralization procedure that is safe and mitigates corrosion should be followed.

3.62.7 Inspection and Monitoring

a) Localized corrosion due to sulfuric acid can be detected and measured by UT and RT.

b) Permanently mounted thickness monitoring sensors can be used.

c) Corrosion can be monitored with coupons and ER probes.

d) To avoid potential corrosion from clean-out of vessels containing concentrated H_2SO_4, they should be considered for non-intrusive inspection. When clean-out is performed, inspection should be considered after clean-out to ensure no significant damage resulted from the cleaning process.

3.62.8 Related Mechanisms

None.

3.62.9 References

1. NACE Publication 5A151, *Materials of Construction for Handling Sulfuric Acid*, NACE International, Houston, TX, 1985.

2. S.W. Dean and G.D. Grab, "Corrosion of Carbon Steel by Concentrated Sulfuric Acid," Paper No.147, *Corrosion/84*, NACE International, Houston, TX.

3. S.K. Brubaker, "Materials of Construction for Sulfuric Acid," *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, pp. 243–258.

4. API Recommended Practice 581, *Risk-Based Inspection Methodology,* American Petroleum Institute, Washington, DC.

5. *Corrosion Control in the Refining Industry*, NACE Course Book, NACE International, Houston, TX, 1999.

6. NACE Standard SP0294, *Design, Fabrication, and Inspection of Storage Tank Systems for Concentrated Fresh and Process Sulfuric Acid and Oleum at Ambient Temperatures*, NACE International, Houston, TX.

7. M. Davies, "Materials Selection for Sulfuric Acid," MTI Publication No. MS-1, Materials Technology Institute of the Chemical Processes Industries, St. Louis, MO.

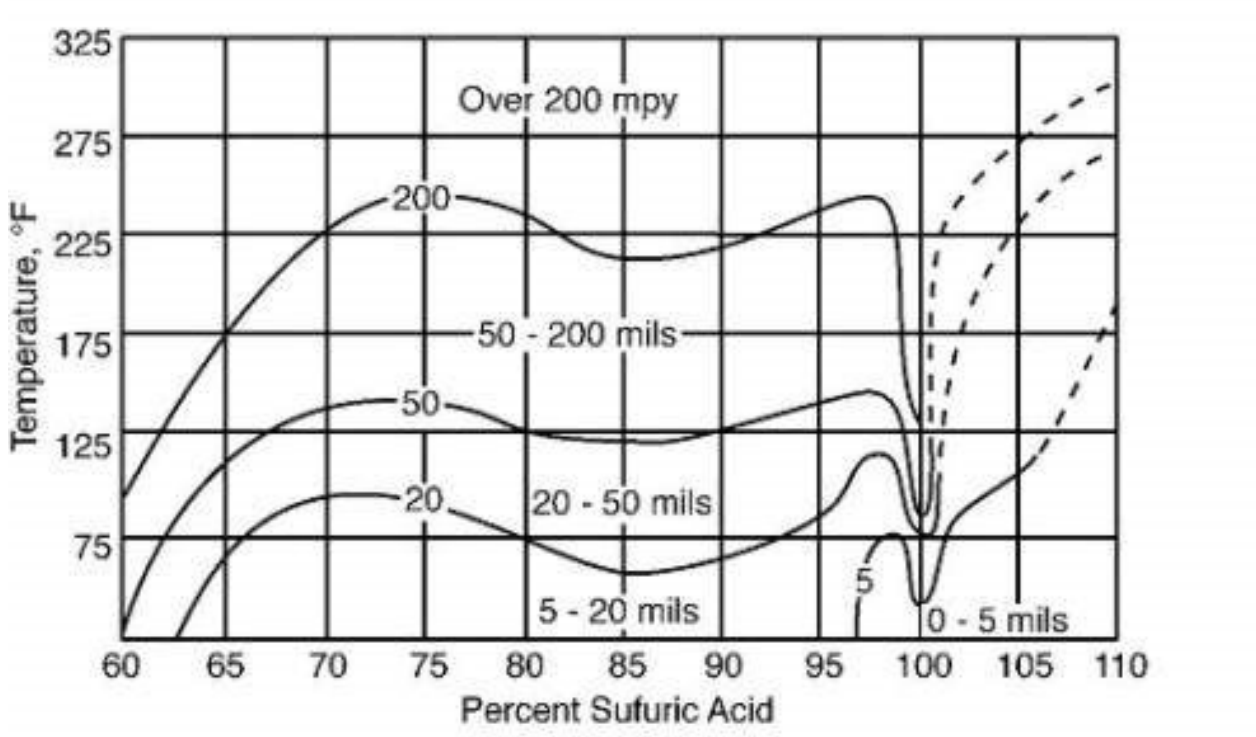

Figure 3-62-1—Sulfuric acid corrosion rate chart for carbon steel.

Figure 3-62-2—Accelerated sulfuric acid corrosion under a baffle.

Figure 3-62-3—Grooving corrosion in the carbon steel vapor line from an alkaline water wash drum in a sulfuric acid alkylation unit.

3.63 Temper Embrittlement

3.63.1 Description of Damage

Temper embrittlement is the reduction in fracture 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 (345 °C to 575 °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.

3.63.2 Affected Materials

a) Primarily 2.25Cr-1Mo low-alloy steel, 3Cr-1Mo (to a lesser extent), and the HSLA Cr-Mo-V rotor steels.

b) Older generation 2.25Cr-1Mo materials manufactured prior to 1972 may be particularly susceptible. Some HSLA steels are also susceptible.

c) The C-0.5Mo, 1Cr-0.5Mo, and 1.25Cr-0.5Mo alloy steels are not as 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.

3.63.3 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 can also have an effect.

c) Temper embrittlement of 2.25Cr-1Mo steels develops more quickly at 900 °F (480 °C) than in the 800 °F to 850 °F (425 °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 material toughness may be required depending on the flaw type and the severity of the operating conditions (e.g. the pressure and stress state), particularly in hydrogen service.

3.63.4 Affected Units or Equipment

a) Temper embrittlement occurs in a variety of process units after long-term exposure to temperatures above 650 °F (345 °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 units (reactors), coker units, and visbreaking units.

c) Welds in potentially susceptible equipment are often more susceptible than the base metal.

3.63.5 Appearance or Morphology of Damage

a) Temper embrittlement is a metallurgical change that is not readily apparent but can be confirmed through (destructive) 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 CVN impact test, as compared to the non-embrittled or de-embrittled material. (Figure 3-63-1) 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.

3.63.6 Prevention/Mitigation

a) Existing materials.

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

2. To minimize the possibility of brittle fracture during start-up and shutdown, many refiners use a pressurization sequence to limit system pressure to about 25 % of the maximum design pressure for temperatures below a minimum pressurization temperature (MPT).

   NOTE The MPT might not be a single temperature but rather a pressure-temperature curve that defines safe operating conditions to minimize the likelihood of brittle fracture.

3. MPTs generally range from 350 °F (170 °C) for the earliest, most highly temper embrittled steels, down to 125 °F (50 °C) or lower for newer, temper-embrittlement-resistant steels (as required to also minimize effects of HE).

4. In addition to controlling pressure and temperature during start-up and shutdown, temper embrittlement needs to be considered in order to prevent brittle fracture when hydrotesting susceptible equipment.

5. If weld repairs are required, the effects of temper embrittlement can be temporarily reversed (the metal can be de-embrittled) by heating at 1150 °F (620 °C) for 2 hr per 1 in. (25 mm) of thickness and rapidly cooling to room temperature. Re-embrittlement will occur over time if the material is re-exposed to the embrittling temperature range.

b) New materials.

1. 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.

2. 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:

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

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

3. 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.

4. 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:

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

5. Expert metallurgical advice should be solicited to determine acceptable composition, toughness, and strength levels, as well as appropriate welding, fabrication, and heat treating procedures for new low-alloy steel heavy wall equipment operating in the temper embrittlement or creep range.

3.63.7 Inspection and Monitoring

a) Inspection is not normally used to detect temper embrittlement, but awareness of susceptible equipment can help prevent future damage.

b) A 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 establish and monitor 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.

c) Process conditions should be carefully monitored to ensure that a proper pressurization/temperature sequence is followed to help prevent brittle fracture due to temper embrittlement. This includes both start-up and shutdown and also applies to the hydrotesting of equipment.

3.63.8 Related Mechanisms

Brittle fracture (3.11).

3.63.9 References

1. R.A. Swift, “Temper Embrittlement in Low-alloy Ferritic Steels,” Paper No. 125, *Corrosion/76*, NACE International, Houston, TX.

2. R.A. White and E.F. Ehmke, *Materials Selection for Refineries and Associated Facilities*, NACE International, Houston, TX, 1991, pp. 53–54.

3. R. Viswanathan, *Damage Mechanisms and Life Assessment of High-temperature Components*, ASM International, 1989.

4. API Recommended Practice 934-A, *Materials and Fabrication of 2¼Cr-1Mo, 2¼Cr-1Mo-¼V, 3Cr-1Mo, and 3Cr-1Mo-¼V Steel Heavy Wall Pressure Vessels for High-temperature, High-pressure Hydrogen Service*, American Petroleum Institute, Washington, DC.

5. API Technical Report 934-B, *Fabrication Considerations for Vanadium-Modified Cr-Mo Steel Heavy Wall Pressure Vessels*, American Petroleum Institute, Washington, DC, April 2011.

6. API Recommended Practice 934-C, *Materials and Fabrication of 1¼Cr-½Mo Steel Heavy Wall Pressure Vessels for High-pressure Hydrogen Service Operating at or Below 825 °F (441 °C)*, American Petroleum Institute, Washington, DC.

7. API Technical Report 934-D, *Technical Report on the Materials and Fabrication Issues of 1¼Cr-½Mo and 1Cr-½Mo Steel Pressure Vessels*, American Petroleum Institute, Washington, DC, First Edition, September 2010.

8. API Recommended Practice 934-E, *Recommended Practice for Materials and Fabrication of 1¼Cr-½Mo Steel Pressure Vessels for Service Above 825 °F (440 °C)*, American Petroleum Institute, Washington, DC.

9. P. Toussaint et al., “Effect of Aging and Hydrogen on Fracture Mechanics and CVN Properties of 2.25Cr-1Mo Steel Grades—Application to MPT Issues,” Paper No. 09341, Corrosion/2009, NACE International, Houston, TX.

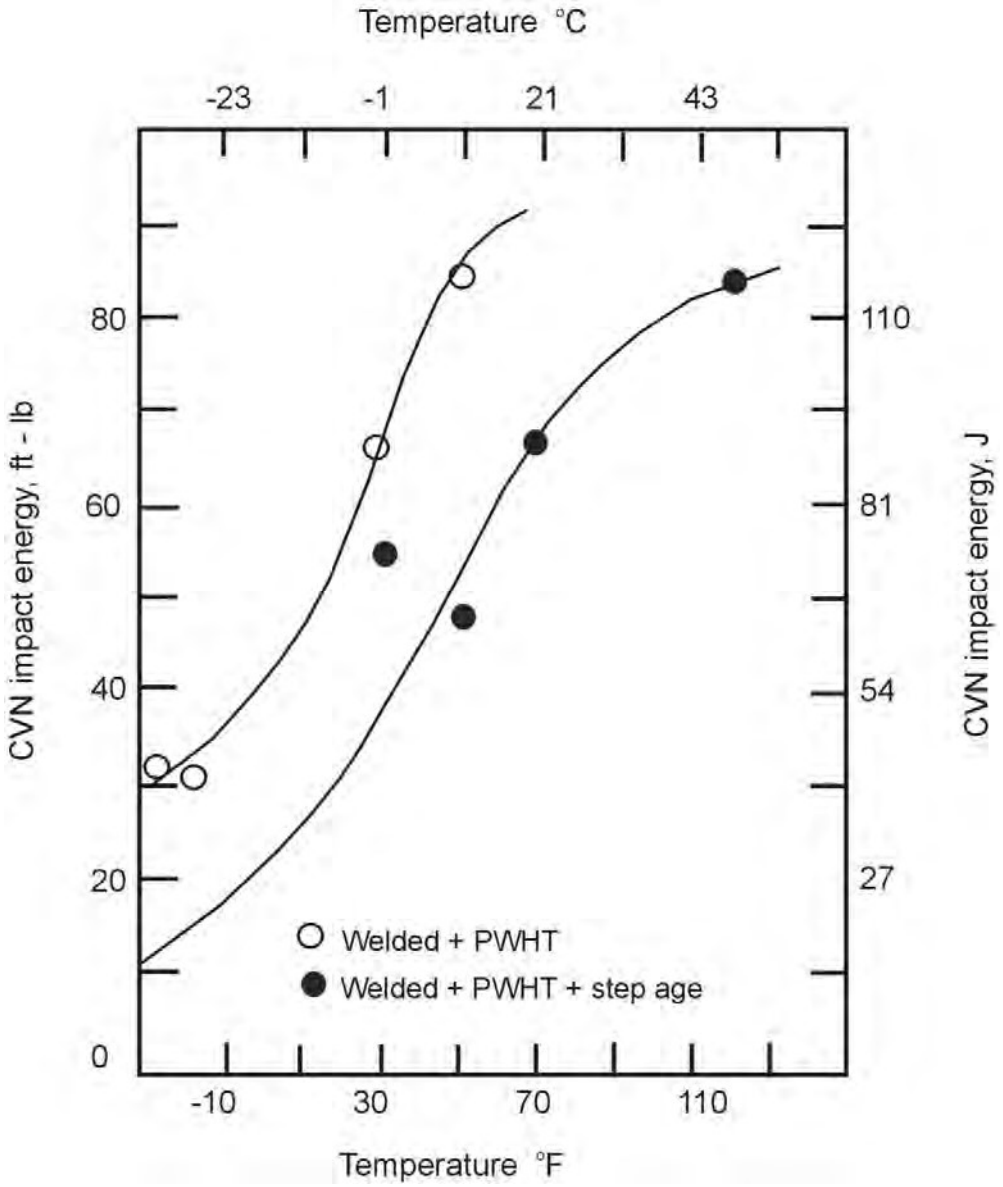

Figure 3-63-1—Plot of CVN toughness as a function of temperature showing an upward shift in the Charpy curve and the 40-ft-lb transition temperature as a result of temper embrittlement.

3.64 Thermal Fatigue

3.64.1 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 during repeated thermal cycling.

3.64.2 Affected Materials

All materials of construction.

3.64.3 Critical Factors

a) Key factors affecting thermal fatigue are the magnitude of the temperature swing and the frequency [number of thermal cycles per second (or minute or day, etc.)].

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

c) Since there are many variables that can affect where and whether thermal fatigue cracking will occur, it is not possible to define a specific, universal limit on allowable temperature swings. For example, rigid attachments may only require a relatively small temperature differential to promote cracking. However, as a reasonable rule of thumb, cracking may be suspected if the temperature swings exceed about 200 °F to 300 °F (110 °C to 165 °C).

d) Damage is promoted by inflexibility to accommodate differential expansion. It 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, e.g. from cold water impinging on a hot tube.

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.

f) In some cases, depending on the frequency at which equipment or an entire unit is shut down and started up, start-up and shutdown can increase the susceptibility to thermal fatigue cracking.

3.64.4 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 or attemporating equipment. (Figure 3-64-1 and Figure 3-64-2)

b) Thermal fatigue cracking has been a major problem in coke drum shells. Thermal fatigue cracking can also occur on coke drum skirts where stresses are promoted by a variation in temperature between the drum and skirt. (Figure 3-64-3 and Figure 3-64-4)

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 in heaters or boilers 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.

3.64.5 Appearance or Morphology of Damage

a) Thermal fatigue cracks usually initiate on the surface of the component, on either the ID or OD surface. 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 3-64-5 and Figure 3-64-6) 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 riser. 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 3-64-7 and Figure 3-64-8)

3.64.6 Prevention/Mitigation

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

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

2. Controlled rates of heating and cooling during start-up and shutdown of equipment can lower stresses.

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

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

1. In steam-generating equipment, slip spacers should slip and rigid attachments should be avoided.

2. 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.

3.64.7 Inspection and Monitoring

a) NDE methods used to detect surface-breaking cracks using same-side inspection include:

1. PT,

2. MT,

3. WFMT,

4. ECT,

5. ACFM, and

6. EMAT.

b) NDE methods used to detect surface-breaking cracks using opposite-side inspection and/or areas that are same side but not accessible include angle beam UT (SWUT or PAUT) and TOFD.

c) AET can be used for continuous monitoring or monitoring during thermal transitions to detect mechanical energy released from cracks when strain values are elevated. Strain value elevation causing thermal fatigue cracking can occur during increase or decrease of temperatures.

d) Temperature monitoring can be performed by installing thermocouples, where practical, on components with thick sections or that are otherwise susceptible to thermal fatigue cracking. The heating and cooling rates should be controlled to avoid steep temperature gradients.

3.64.8 Related Mechanisms

Mechanical fatigue (3.43), corrosion fatigue (3.21), and DMW cracking (3.26).

3.64.9 References

1. *Steam—Its Generation and Use*, 40th Edition, Babcock & Wilcox, 1992.

2. *Combustion: Fossil Power Systems*, Third Edition, Combustion Engineering, Windsor, CT, 1981.

3. H. Thielsch, *Defects and Failures in Pressure Vessels and Piping*, Krieger Publishing, Malabar, FL, 1977.

4. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991.

5. D.N. French, *Metallurgical Failures in Fossil Fired Boilers*, John Wiley and Sons, New York, NY, 1993.

6. B. Dooley and W. McNaughton, *Boiler Tube Failures: Theory and Practice*, 3 Volumes, EPRI, 1995.

Figure 3-64-1—Thermal fatigue cracks on the inside of a heavy wall SS pipe downstream of cooler H_2 injection into a hot hydrocarbon line.

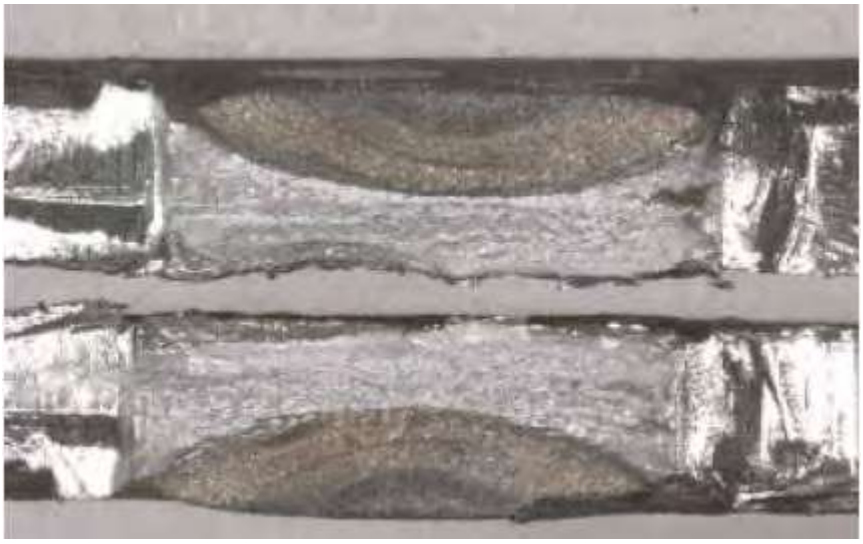

Figure 3-64-2—Thermal fatigue cracking surfaces of 304L stainless steel at a mix point in the BFW preheater bypass line around the high-temperature shift effluent exchanger in a hydrogen reformer. The delta T is 325 °F (180 °C) at an 8-in. bypass line tying into a 14-in. line. Failure occurred 3 years after start-up.

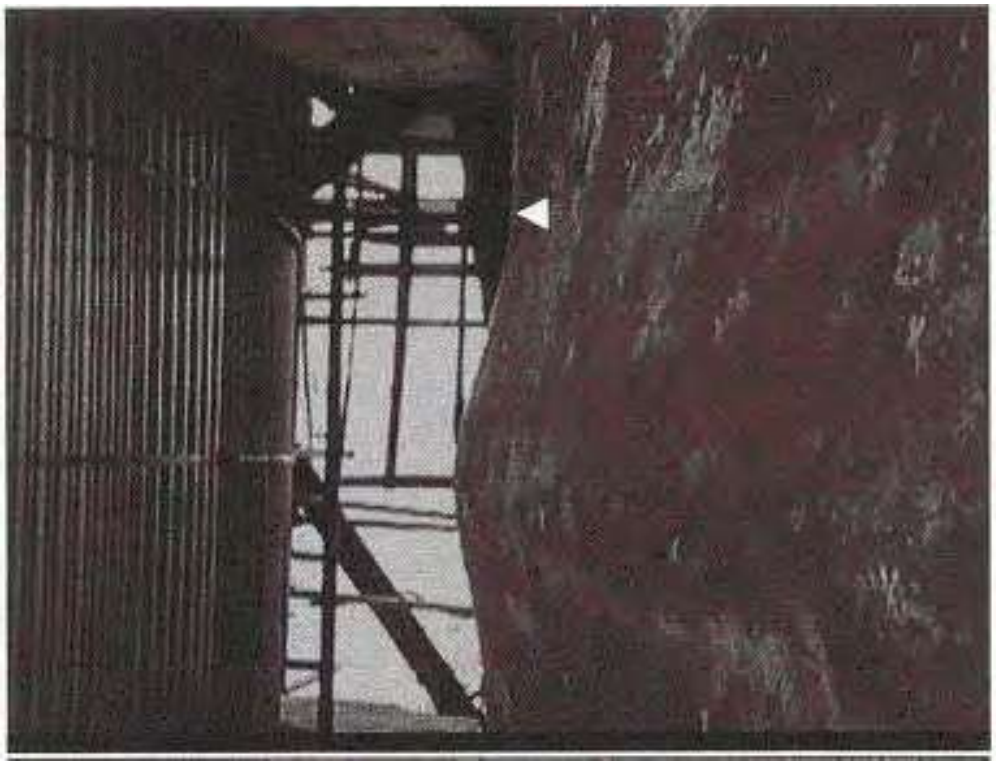

Figure 3-64-3—Bulging in a skirt of a coke drum due to thermal cycling from coker operation.

Figure 3-64-4—Thermal fatigue cracking associated with bulged skirt shown in Figure 3-64-3.

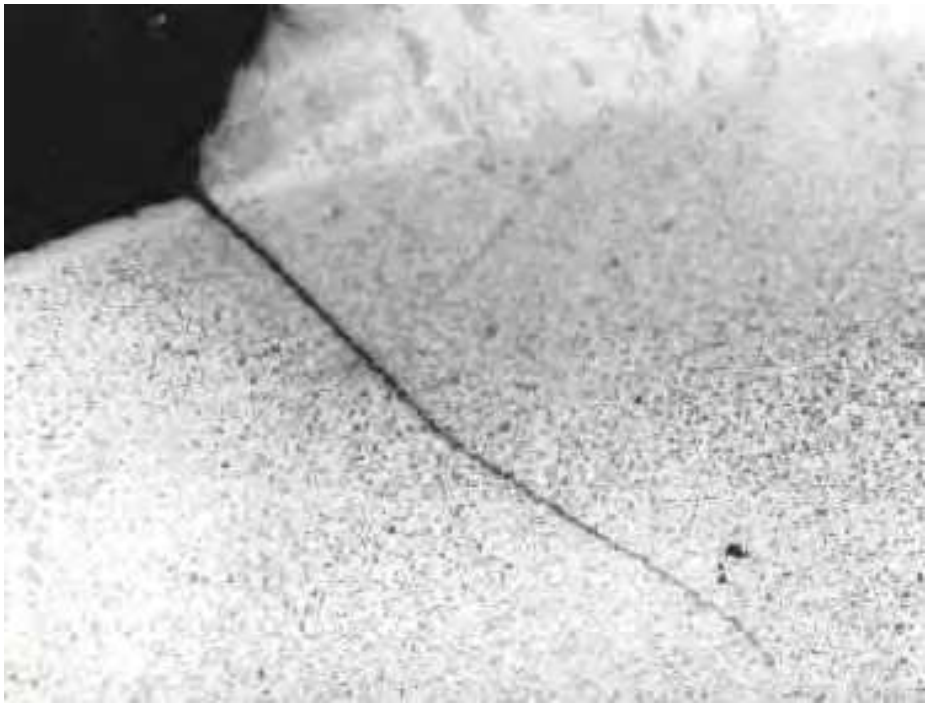

Figure 3-64-5—Metallographic section through a thermal fatigue crack in a carbon steel sample indicates origin at the toe of an attachment weld. Magnification 50X, etched.

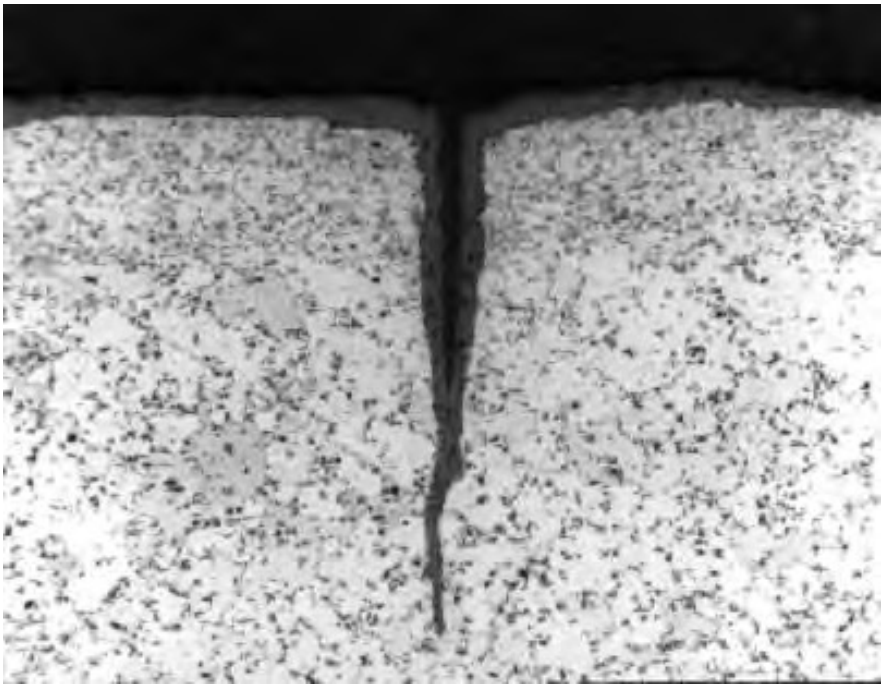

Figure 3-64-6—Cracks that develop over time will typically fill with oxide, may stop and restart (note jog part way along the crack), and do not necessarily require a change in section thickness to initiate the crack. Magnification 100X, etched.

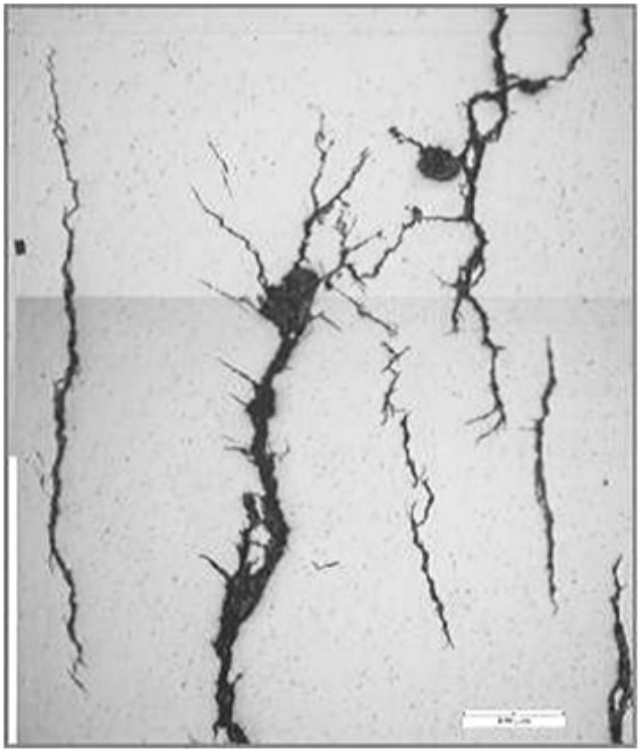

Figure 3-64-7—Metallographic cross section of a superheated steam outlet line that failed from thermal fatigue. Unetched.

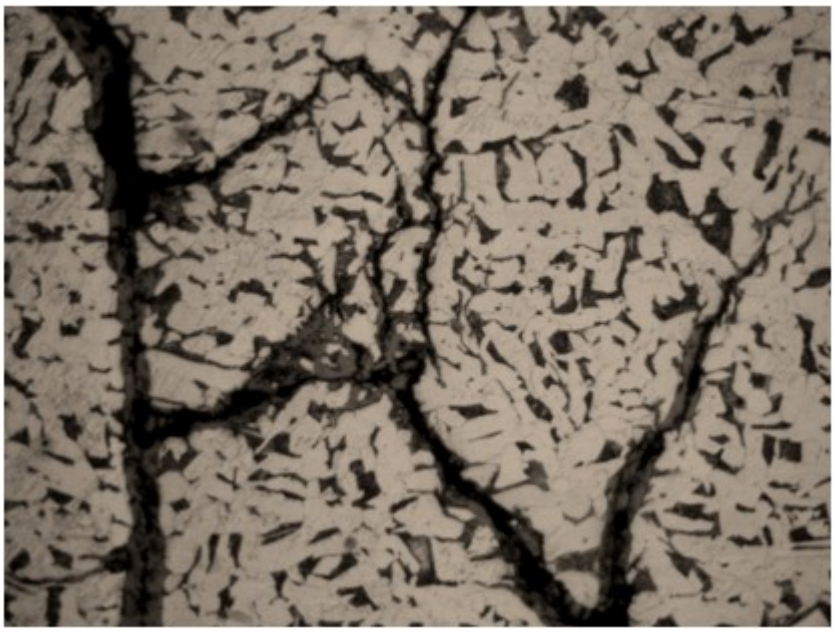

Figure 3-64-8—Photomicrograph of the same failed superheated steam outlet line shown in Figure 3-64-7. Etched.

3.65 Thermal Shock

3.65.1 Description of Damage

Thermal shock cracking can occur when high and non-uniform thermal stresses develop in a single event over a 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 cracking usually occurs when a much colder liquid contacts a much warmer metal surface. In refining, the concern generally arises after a large equipment fire is extinguished using fire water.

3.65.2 Affected Materials

All metals and alloys.

3.65.3 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) Stainless steels have higher coefficients of thermal expansion than carbon and alloy steels or nickel-based alloys and are more likely to see higher stresses.

c) High-temperature exposure during a fire followed by water quench to extinguish the fire can result in thermal shock cracking.

d) Large and rapid temperature changes that can result from water quenching as a result of rain deluges could cause thermal shock cracking.

e) Fracture is related to constraint on a component that prevents the component from expanding or contracting with a change in temperature. The metal surrounding a locally quenched area of the metal can provide the necessary constraint.

f) Cracking in cast components such as valves may initiate at casting flaws and progress through the thickness.

g) It is more prevalent in thick sections that can develop high thermal gradients.

3.65.4 Affected Units or Equipment

a) FCC, coker, 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) Heavy wall machinery, typically made of thick castings, can be affected, particularly those made of high-chromium steels such as 12Cr.

d) Materials that have lost ductility, such as Cr-Mo equipment (due to temper embrittlement), are particularly susceptible to thermal shock.

e) Equipment subjected to accelerated cooling procedures to minimize shutdown time is potentially subject to thermal shock cracking.

3.65.5 Appearance or Morphology of Damage

Surface initiating cracks may also appear as “craze” cracks.

3.65.6 Prevention/Mitigation

a) Minimize situations where rain or fire-water deluge can contact hot equipment.

b) Design to minimize severe restraint in hot equipment that can potentially get severely quenched.

c) Install thermal sleeves or other protective measures to prevent inadvertent cold liquid impingement on hot pressure boundary components.

3.65.7 Inspection and Monitoring

a) This type of damage is uncommon, but when it occurs it results in highly localized cracking that may be difficult to locate. Since it mostly occurs as a single, unpredictable event, e.g. a fire, severe storm, or major excursion or upset, it is not amenable to regular inspection monitoring. Methods to detect cracking resulting from thermal shock include:

1. VT (may reveal cracking, but it might be difficult to differentiate actual cracks in the metal from superficial craze cracks in the oxide layer);
2. PT;
3. MT; and
4. UT.

3.65.8 Related Mechanisms

Thermal fatigue (3.64) and short-term overheating—stress rupture (3.55).

3.65.9 References

1. *ASM Handbook—Failure Analysis and Prevention*, Volume 11, ASM International, Materials Park, OH.

2. API 579-1/ASME FFS-1, *Fitness-For-Service*, American Petroleum Institute, Washington, DC.

3.66 Titanium Hydriding

3.66.1 Description of Damage

Hydriding of titanium is a metallurgical phenomenon in which hydrogen diffuses into the titanium and reacts to form an embrittling hydride phase. This can result in a complete loss of ductility and fracture toughness, potentially enabling a brittle fracture, with no noticeable sign of corrosion or loss in thickness.

3.66.2 Affected Materials

Titanium and titanium alloys.

3.66.3 Critical Factors

a) The critical factors are metal temperature, solution chemistry, and alloy composition.

b) This is a phenomenon that occurs in specific environments at temperatures above 165 °F (75 °C) and at a pH below 3, pH above 8, or neutral pH with high H_2S content.

c) Galvanic contact between titanium and more active materials such as carbon steel and 300 series SS promotes damage. However, hydriding can occur in the absence of a galvanic couple.

d) Embrittlement occurs over a period of time as hydrogen is absorbed by the component and reacts to form an embrittling hydride phase. The depth and extent of hydriding will continue to increase until a complete loss of ductility results.

e) Hydriding has also occurred in some environments as a result of the corrosion of steel that was accidentally embedded into the surface of the titanium during fabrication.

f) Iron sulfide scale formed from the corrosion of steel in upstream units and equipment can be carried into titanium equipment and cause hydrogen pickup and resulting hydriding.

g) The solubility of hydrogen in pure titanium and alpha-beta titanium alloys (e.g. Gr. 2. Gr. 7, Gr 12, and Gr. 16) is limited to 50 ppm to 300 ppm. When the hydrogen concentration exceeds this solubility limit, hydride is formed. Beta alloys are more tolerant of hydrogen, and 2000 ppm can be absorbed without causing detrimental hydriding. However, beta alloys are not typically used for refinery process equipment.

3.66.4 Affected Units or Equipment

a) Titanium has mainly been used in heat exchangers and air coolers, primarily to take advantage of the corrosion resistance of titanium tubes in these services. Damage has occurred primarily in SWSs and amine units in the overhead condensers or air coolers and other heat exchanger tubes, as well as some piping and other titanium equipment operating above about 165 °F (75 °C). In most cases, cracking has occurred during maintenance operations, e.g. turnarounds, rather than while the equipment was in service.

b) Hydriding can also occur in hydrogen atmospheres at temperatures > 350 °F (175 °C), especially in the absence of moisture or oxygen.

c) Cathodic protection potentials less −0.9 v SCE on titanium equipment can promote hydrogen entry and hydriding.

3.66.5 Appearance or Morphology of Damage

a) Titanium hydriding is a metallurgical change that is not visually apparent and can only be confirmed through metallurgical examination (Figure 3-66-2 and Figure 3-66-3) or mechanical testing.

b) The detrimental result of titanium hydriding is cracking, which will be visually apparent. (Figure 3-66-1)

    1. When leaks or cracking in titanium pressure retaining parts occur, titanium hydriding is likely to be anticipated as the cause, and the leaks will likely be obvious.

c) Heat exchanger tubes that have become embrittled may remain intact until disturbed by removal of the bundle for inspection. The tubes crack as the bundle flexes when it is removed.

d) Cracking can occur if there is an attempt to re-roll tube ends that have become embrittled.

e) Another possible ramification that has occurred is ignition and burning of titanium tubes.

    1. Titanium is a reactive metal that can combust in the presence of heat and oxygen. Caution should be exercised when exposing titanium to heat or flame during downtimes. Exposure to pyrophoric materials or cutting torches has resulted in metal fires.

3.66.6 Prevention/Mitigation

a) The risk of failure due to titanium hydriding should be considered in known hydriding services such as amine or SWS overhead condensers.

b) Precautions should be taken during outages to avoid brittle fracture of titanium components, e.g. air cooler tubes, when used in known hydriding services.

c) Where galvanic contact has promoted hydriding, the problem can be avoided by using all titanium construction or by electrically isolating the titanium from non-titanium components. Eliminating the galvanic couple may not prevent hydriding in alkaline SW environments.

3.66.7 Inspection and Monitoring

a) Cracks resulting from titanium hydriding are typically found through VT.

b) Sampling and destructive testing using microstructural analysis and/or mechanical testing methods are typically required to confirm the presence and degree of hydriding.

c) NDE techniques are generally not employed in refining to detect hydriding. Rather, sampling and destructive testing are used when there is a need to determine whether hydriding has occurred.

d) Embrittlement can be confirmed by a bend, crush, or impact (hammer) test in a vice. Unaffected titanium will be crushed or bent in a ductile fashion while embrittled components will crack or shatter (sometimes like glass) with little or no sign of ductility.

e) ECT techniques have been used in other industries, e.g. in the power and aircraft industries, to detect both the presence of hydriding as well as cracks within the hydrided layer of components. Because of the effect on eddy current response of the change in electrical resistivity caused by hydriding, hydriding may appear as, and be misinterpreted as, wall thinning.

    1. With no track record of use in oil refinery equipment, such techniques should be used with caution, including validation of the technology and methodology.

3.66.8 Related Mechanisms

Hydriding is a damage mechanism that is unique to a few materials including alloys of titanium and zirconium. However, it is considered a form of HE (3.40) and could result in a brittle fracture (3.11).

3.66.9 References

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Figure 3-66-1—Titanium heat exchanger tube that failed from hydriding in a SW cooler. The cooling medium was seawater.

Figure 3-66-2—High-magnification photomicrograph of a cross section of the tube shown in Figure 3-66-1 through the crack tip. Magnification 200X.

Figure 3-66-3—Another high-magnification photomicrograph of a cross section of the tube in Figure 3-66-1, showing more of the cross section through the tip of the crack. Titanium hydrides are more clearly discernable. Magnification 400X.

3.67 Wet H_2S Damage (Blistering/HIC/SOHIC/SSC)

3.67.1 Description of Damage

This section describes four types of damage that result in blistering and/or cracking of carbon steel, one of which also affects low-alloy steels and some other high-strength or hardenable materials, in wet H_2S environments.

a) Hydrogen Blistering

Hydrogen blisters form bulges primarily on the ID surface of pressure vessels. Hydrogen blistering is rare in seamless pipe but can occur in seam-welded pipe. Blisters are caused by the hydrogen atoms that form on the surface of the steel as a result of corrosion reactions. Sulfur acts as a *recombination poison*, delaying the combining of hydrogen atoms into hydrogen gas molecules (H_2), allowing the hydrogen atoms to linger on the steel surface. The small hydrogen atoms can then readily diffuse into the steel. (This *hydrogen charging* effect applies to all types of wet H_2S damage.) The hydrogen atoms diffusing into the steel collect at discontinuities such as inclusions or laminations, where they then combine to form H_2 gas, because there is no recombination poison within the steel to inhibit the reaction. The hydrogen gas molecules thus become trapped at the site because they are too large to diffuse away through the steel. As corrosion proceeds, hydrogen atoms continue to form on the surface and then diffuse into the steel to become trapped as H_2 at the collection sites, building the H_2 gas pressure to the point where local deformation occurs, forming a blister. Blistering only results from hydrogen generated by corrosion, not from hydrogen gas in the process stream. (See Figure 3-67-1 and Figure 3-67-2 for blistering damage.)

HCN accentuates the problem by weakening protective films on the metal surface, thereby increasing the rate of corrosion. This in turn leads to increased hydrogen charging and associated wet H_2S damage. (This also applies to all types of wet H_2S damage.)

b) Hydrogen-induced Cracking (HIC)

HIC results from the same cause as blistering, i.e. from hydrogen atoms diffusing into the steel as a result of corrosion. However, in this case, when the hydrogen atoms diffuse into the steel, rather than forming blisters, internal separations parallel to the surface of the steel result. Again, it is the pressure buildup resulting from hydrogen atoms combining to form H_2 gas that cause the internal separations within the wall of the vessel. The separations are initially microscopic in size but can connect together to form macroscopic-sized cracks, by growing into one large separation on the same plane parallel to the surface or more commonly by linking up with HIC on different planes (at different depths into the wall), eventually forming a thru-wall leak path. Interconnecting cracks between HIC separations on different planes have a stair step appearance, and so HIC is sometimes referred to as “stepwise cracking.” (See Figure 3-67-3 to Figure 3-67-5 for HIC damage.)

c) Stress-oriented Hydrogen-induced Cracking (SOHIC)

SOHIC results from an array of HIC (separations or cracks) stacked on top of each other. When acted upon by a high stress level (residual or applied), the stacked HIC will connect and create a thru-thickness crack that is perpendicular to the surface. SOHIC most often occurs in the base metal adjacent to weld HAZs, the residual stress from welding being the most common driver of SOHIC. SOHIC can initiate from the stacked HIC alone, from sulfide stress cracks, or from other crack-like defects or stress concentrations. SOHIC is a potentially more damaging form of cracking than HIC because of its relatively higher rate of developing a thru-wall crack. In addition, an absence of visual blistering may leave a false sense of security that H_2S damage is not active, yet subsurface SOHIC may be present. (See Figure 3-67-6 to Figure 3-67-8 for SOHIC damage.)

d) Sulfide Stress Cracking (SCC)

SSC is the cracking of a susceptible metal under the combined action of tensile stress and corrosion in the presence of water and H_2S. SSC is a form of HE cracking (see 3.40) resulting from absorption of atomic hydrogen that is produced on the metal surface by the corrosion process. In addition to carbon steel and low-alloy steels, martensitic stainless steels such as Type 410 are also susceptible if hardness is not controlled to a low enough level.

SSC occurs in high-strength (high-hardness) steels but can also initiate in highly localized zones of high hardness in weld metal and HAZs. While SSC is uncommon in modern (post-1980) steels, zones of high hardness can sometimes be found in weld cover passes and attachment welds that are not tempered (softened) by subsequent passes. PWHT is beneficial in reducing the high hardness and residual stresses that render steel susceptible to SSC and is essential when welding hardenable low-alloy steels including Cr-Mo steels, as well as martensitic stainless steels. Some carbon steels contain REs that form hard areas in the HAZ that will not temper at normal stress-relieving temperatures. Using preheat helps minimize these hardness problems. While high-strength steels are susceptible to SSC, they are only used in limited applications such as valve internals and similar internal components in the refining industry.

Hard welds and hard spots within otherwise soft welds can arise with SAW when an active flux is used along with high welding voltage. This high hardness can lead to SSC. (See Reference 9.)

The time to failure by SSC decreases as the steel strength, level of tensile stress, and hydrogen charging potential of the environment increase. (See Figure 3-67-9 and Figure 3-67-10 for SSC damage.)

3.67.2 Affected Materials

Carbon steel, and in the case of SSC, low-alloy steels, and martensitic stainless steels.

3.67.3 Critical Factors

a) A liquid water phase containing H_2S, i.e. a *sour environment*, must be present and must contact the steel in order for wet H_2S damage to occur. (Equipment highly susceptible to SSC can fail even during short SW excursions such as might be encountered during equipment shutdowns.) Beyond this, the critical factors that affect and differentiate the various forms of wet H_2S damage are environmental conditions (H_2S level, pH, contaminants, and temperature), material properties [microstructure and hardness (which correlates to strength)], and tensile stress level (applied or residual).

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

c) H_2S level.

1. Hydrogen permeation increases with increasing H_2S partial pressure due to a concurrent increase in the H_2S concentration in the water phase.

2. A value of 50 ppmw H_2S in the water phase is often stated as the minimum concentration where wet H_2S damage can occur. 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 ppmw of H_2S in the water has been found to be sufficient to cause hydrogen charging of the steel.

3. Susceptibility to SSC increases with increasing H_2S partial pressure in the gas phase, as long as there is a water phase present concurrently. An H_2S partial pressure above about 0.05 psia (0.0003 Mpa) can cause SSC in steels with a tensile strength above about 90 ksi (620 MPa), in steels with localized zones of weld or weld HAZ hardness above 237 HB, or in non-PWHT'd or inadequately PWHT'd Cr-Mo steel welds. This partial pressure value is based primarily on oilfield experience and is not exact. The H_2S partial pressure to cause SSC will vary depending on other contributing factors, including steel strength and hardness, pH, and stress level.

d) pH.

1. Hydrogen permeation and diffusion rates in steel have been found to be minimal at pH 7 and increase at both higher and lower pH.

2. Decreasing pH below 7 increases the potential for wet H_2S damage. At pH < 4, only a small amount (ppm levels) of H_2S is needed. However, wet H_2S damage can also occur at pH above 7. If an environment with an alkaline pH is corrosive and contains H_2S, e.g. ammonium bisulfide, wet H_2S damage can still occur.

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

4. Rich amine solutions are also an alkaline environment where wet H_2S damage can occur. See 3.3.

e) Contaminants.

1. Salts or other species in the water phase that decrease the pH or increase the corrosion rate will increase the hydrogen charging rate and, therefore, the severity of the wet H_2S damage environment.

2. HCN in the water phase can cause increased corrosion rates, which significantly increases hydrogen permeation in alkaline (high-pH) SW and thereby increases the potential for all forms of wet H_2S damage. For example, at pH > 7.6 with 20 ppmw dissolved HCN in the water, as little as 1 ppmw total sulfide content in the water can cause SSC.

f) Temperature.

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

2. SSC potential is greatest at about 70 °F (20 °C) and decreases with increasing or decreasing temperature. This is likely related to the rate of diffusion of hydrogen and its behavior in steel at different temperatures. SSC is generally a concern below about 200 °F (95 °C); however, the limiting temperature above which SSC is no longer a concern will depend on the situation, i.e. on the hardness of the steel involved and the severity of other environmental factors such as pH.

   — If susceptible metals become charged with hydrogen during high-temperature exposure [e.g. above 200 °F (95 °C)], they can subsequently crack when cooled back down to ambient.

g) Microstructure.

1. Blistering and HIC are strongly affected by the presence of inclusions and laminations, which provide sites for diffusing hydrogen to accumulate.

   — Flat, elongated manganese sulfide (MnS) inclusions produced by ordinary steel plate rolling practices are particularly detrimental. However, steel chemical composition and manufacturing methods can be tailored to produce HIC-resistant steels. (See Reference 6.)

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

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

h) Hardness.

1. Hardness is primarily an issue with SSC. Blistering, HIC, and SOHIC damage are not related to steel hardness. Typical carbon steels used in refinery applications are not expected to be susceptible to SSC because their strength and hardness is sufficiently low. Welds in carbon steel should be controlled to produce weld hardness < 200 HB, and they will typically achieve this without any special precautions. Carbon steel welds are not susceptible to SSC unless localized zones of hardness above 237 HB are present.

   — The welds in submerged-arc-welded steel pipe where an acid flux and high welding voltage were used can have hard zones sufficiently hard to cause SSC.

2. High-strength steels (generally those with hardness greater than 22 HRC) or steels that can be hardened by welding, such as Cr-Mo steels, can be susceptible to SSC, and steps need to be taken, such as limiting the hardness of the material or applying PWHT to reduce the hardness of the welds, to prevent SSC. (See Reference 8.)

i) Tensile stress level.

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

2. The tensile stress needed to cause SOHIC typically comes from weld residual stresses, which, in the absence of thermal stress relief, are typically very high, i.e. approaching the yield strength. High local stresses or notch-like discontinuities such as shallow sulfide stress cracks can serve as initiation sites for SOHIC. PWHT is somewhat effective in preventing or reducing SOHIC damage.

3. The tensile stress needed to cause SSC in a susceptible material can come from applied stress or residual stress.

   — High-strength components are typically used in the non-welded condition and, therefore, are most likely to fail from applied stress. A highly susceptible material, e.g. one with very high hardness, needs relatively little tensile stress to cause SSC.

   — Hardenable steels that are welded need to be PWHT'd to reduce hardness in order to avoid SSC, and the PWHT will also relieve residual stresses. PWHT (for stress relief) of carbon steel is normally not necessary, but if there is concern for localized hard spots in the HAZ due to the chemical composition of the steel, PWHT will relieve the weld residual stresses even if it does not reduce the hardness of the hard spots, and relief of the residual stresses will help minimize the likelihood of SSC.

3.67.4 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, an ammonium bisulfide concentration above 2 % increases the potential for blistering, HIC, and SOHIC.

c) Cyanides, particularly in the vapor recovery sections of FCC and delayed coking units. significantly increase the probability and severity of blistering, HIC, and SOHIC damage. 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.

d) SWS and amine regenerator overhead systems are especially prone to wet H_2S damage because of generally high ammonia or ammonium bisulfide concentrations and cyanides.

e) SSC is most likely found in hard welds and HAZs and in high-strength components including bolts, relief-valve springs, 400 series SS valve trim, and compressor shafts, sleeves, and springs.

3.67.5 Appearance or Morphology of Damage

a) All four forms of wet H_2S damage are best illustrated though the photos and diagrams shown in Figure 3-67-1 to Figure 3-67-10.

b) Hydrogen blisters appear as bulges, most often on the ID surface of the steel, but can be found anywhere in the shell plate or head of a pressure vessel. Blistering has been found on rare occasions in seamless pipe; however, large-diameter seam-welded pipe, which is typically made from plate, similar to a pressure vessel, will have susceptibility comparable to pressure vessels. Blistering has even been seen in the middle of a weld, but this is very rare.

c) Late-stage HIC or SOHIC will create surface-breaking cracks.

d) In pressure-containing equipment, SOHIC and SSC damage are most often associated with weldments.

e) Blisters and HIC typically are not associated with welds but rather occur within and sometimes throughout a shell plate or course. However, they can grow toward and intersect a weld, which increases the likelihood for SOHIC in the HAZ and development of a thru-wall crack.

3.67.6 Prevention/Mitigation

a) Effective barriers, including alloy cladding and coatings, that separate the surface of the steel from the wet H_2S environment can prevent blistering, HIC, and SOHIC. Barrier coatings can also prevent SSC of the underlying material, but they are often considered a temporary measure until a more permanent solution can be put in place.

b) Process changes that affect the pH of the water phase and/or ammonia or cyanide concentration can help to reduce blistering, HIC, and SOHIC. A common practice is to utilize wash water injection to dilute the HCN concentration, e.g. 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 Reference 6.

d) PWHT can help minimize susceptibility to SOHIC.

e) PWHT will not prevent blistering or HIC, because they are not initiated by stress and usually occur away from and not associated with welds.

f) SSC in welds can generally be prevented by limiting the hardness of carbon steel welds and HAZs to 200 HB maximum. Similar, but slightly higher, maximum hardness limits are normally applied to Cr-Mo steels for which high hardness is prevented by using preheat, PWHT, and welding procedure control.

g) High-strength materials should be selected in accordance with NACE MR0103/ISO 17945.

h) Specialized corrosion inhibitors can be used.

3.67.7 Inspection and Monitoring

a) Process conditions should be monitored and evaluated by process engineers and corrosion or materials specialists to identify 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 blistering is normally done by internal VT.

c) Inspection for SOHIC typically focuses on weld seams and nozzles. For details of inspection plans including methods, coverage, and surface preparation, as well as repair, see Reference 1.

d) Cracks from SOHIC or surface-breaking HIC may be seen visually. However, to enable crack detection at an early stage, WFMT, ECT, or ACFM techniques can be used. Surface preparation by grit blasting, high-pressure water blasting, flapper wheel cleaning, or other method is usually required for WFMT but not for ACFM or ECT. PT cannot find tight cracks and is not reliable for finding SOHIC or HIC.

1. It has become increasingly common to inspect welds on new pressure vessels intended for sour service using WFMT or another high-resolution NDE method. This is done to ensure there are no remaining flaws associated with the welds that would not have been found using standard fabrication inspection protocols when the vessel is first put into service. However, this was not done for most vessels currently in service in refineries. Because of this, extensive inspection on in-service equipment, when similar, high-resolution inspection has not been performed in the past, often leads to finding small, non-growing flaws that likely have been present since initial fabrication and are likely not H_2S damage. Therefore, caution and careful assessment need to be applied.

2. SOHIC occurs in the base metal alongside the weld. If the NDE applied for wet H_2S inspection of welds, i.e. for SOHIC, finds indications in the weld metal, they are likely fabrication weld flaws rather than SOHIC.

e) Angle beam UT techniques including external SWUT and PAUT can be used. These techniques are especially useful for volumetric inspection and crack sizing.

f) Electric resistance instruments are not effective for measuring crack depth.

g) Internal HIC can appear to be deep, clearly defined, individual, sharp-cornered pits when using straight beam UT for thickness measurements on vessel shells or heads. This is caused by the reflection of the ultrasonic sound wave off the internal separation. Practitioners need to be aware of this when interpreting thickness readings on equipment in wet sour service in order to not misinterpret internal HIC as ID pitting.

h) AET can be used to locate cracks and monitor crack growth.

i) If cracking or failure due to SSC is not visually apparent, the cracks can normally be found using MT if they are surface breaking and there is access to the surface, or angle beam UT (SWUT or PAUT) if they are subsurface or on an inaccessible internal surface.

3.67.8 Related Mechanisms

HE (3.40), hydrogen stress cracking in HF acid (3.41), and DMW cracking (3.26). Amine cracking (3.3) and carbonate cracking (3.12) can also occur in wet H_2S environments and may be similar in appearance. They are sometimes confused with wet H_2S damage.

3.67.9 References

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9. D.J. Kotecki and D.G. Howden, *Submerged-arc-weld Hardness and Cracking in Wet Sulfide Service*, WRC Bulletin 184, Welding Research Council, Shaker Heights, OH, 1973.

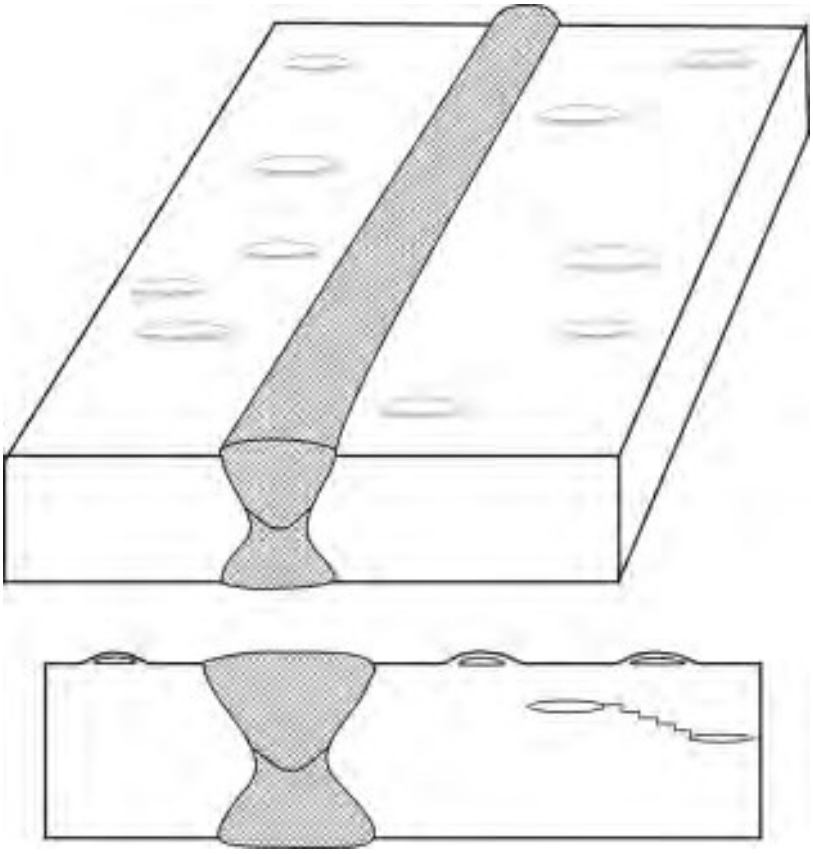

Figure 3-67-1—Illustration showing hydrogen blistering and HIC damage.

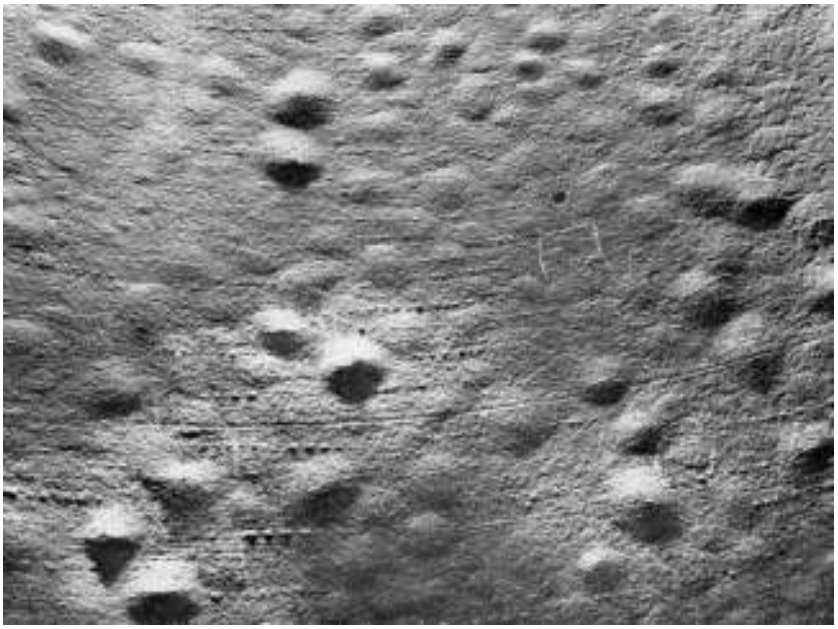

Figure 3-67-2—Extensive hydrogen blistering on the ID surface of a steel pressure vessel.

Figure 3-67-3—HIC damage as shown in the cross section of the shell of a trim cooler that had been cooling vapors off a hot high-pressure separator (HHPS) vessel in a hydroprocessing unit.

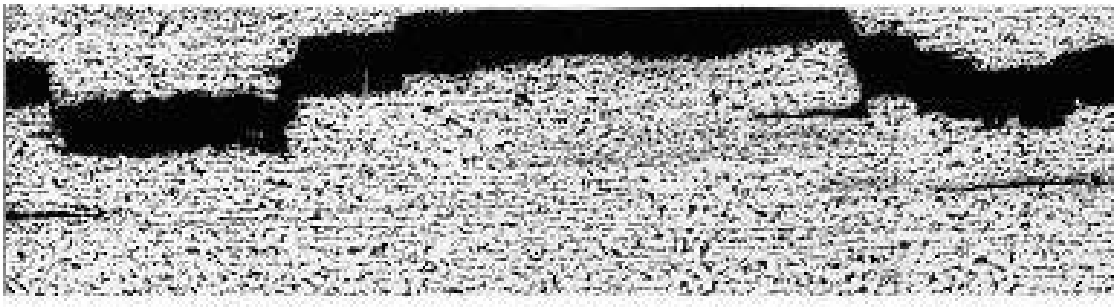

Figure 3-67-4—High-magnification photomicrograph of HIC damage.

Figure 3-67-5—High-magnification photomicrograph showing stepwise cracking nature of HIC damage.

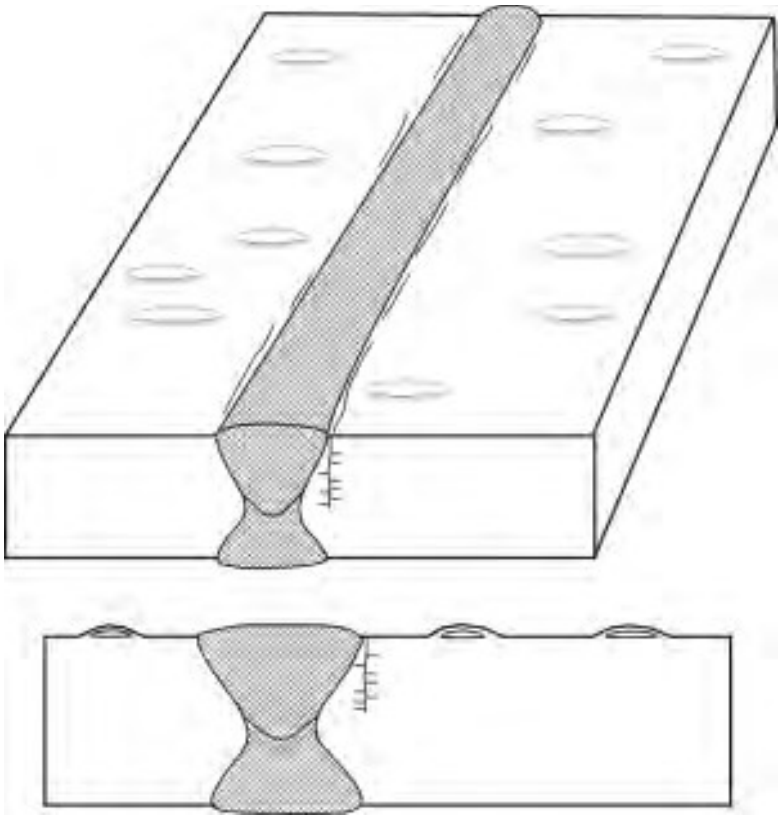

Figure 3-67-6—Illustration of hydrogen blistering that is accompanied by SOHIC damage at the weld.

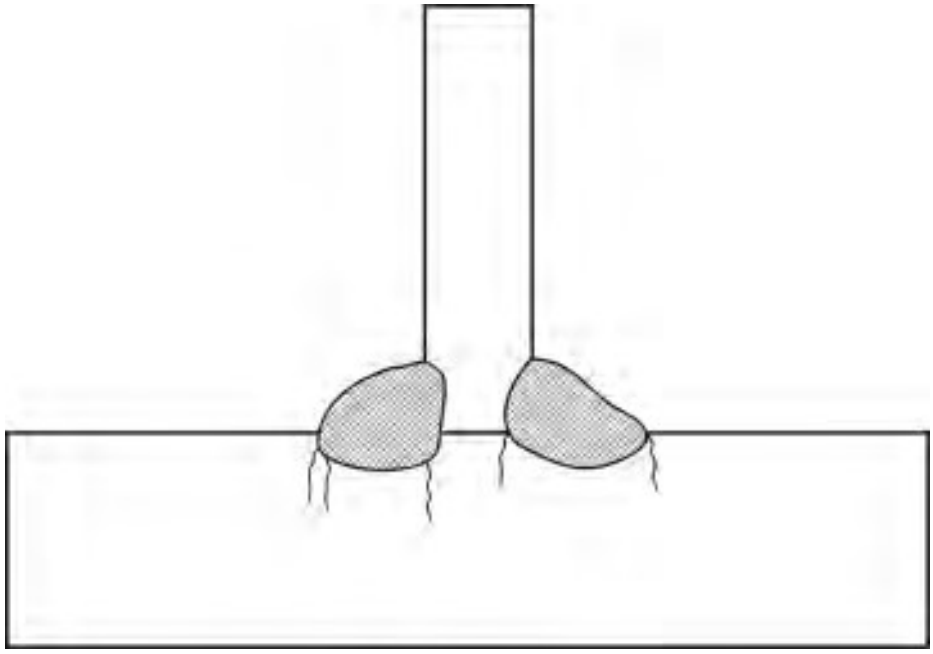

Figure 3-67-7—Illustration of SOHIC damage at a fillet weld that is usually a combination of SSC and SOHIC.

Figure3-67-8—Photograph showing WFMT indication of SOHIC damage.

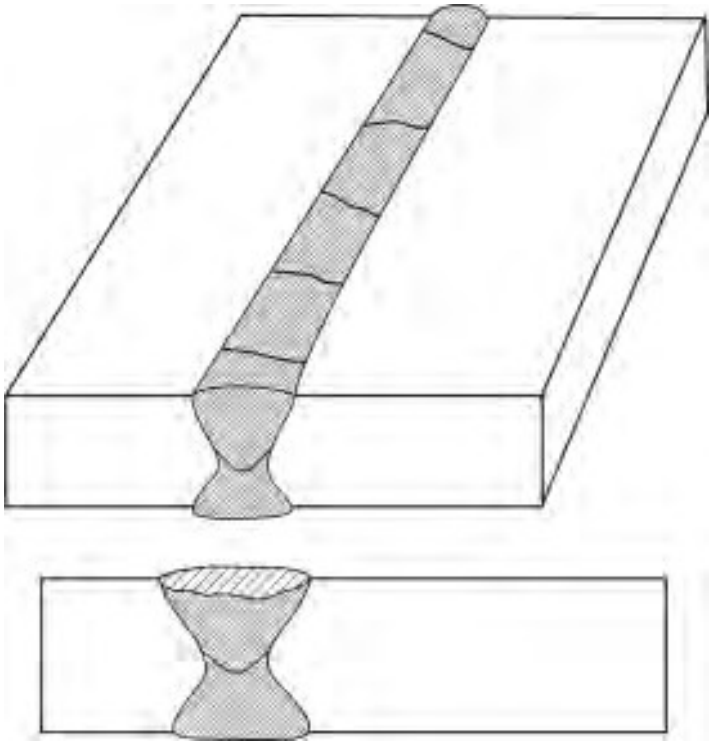

Figure 3-67-9—Illustration of SSC damage in a hard weld.

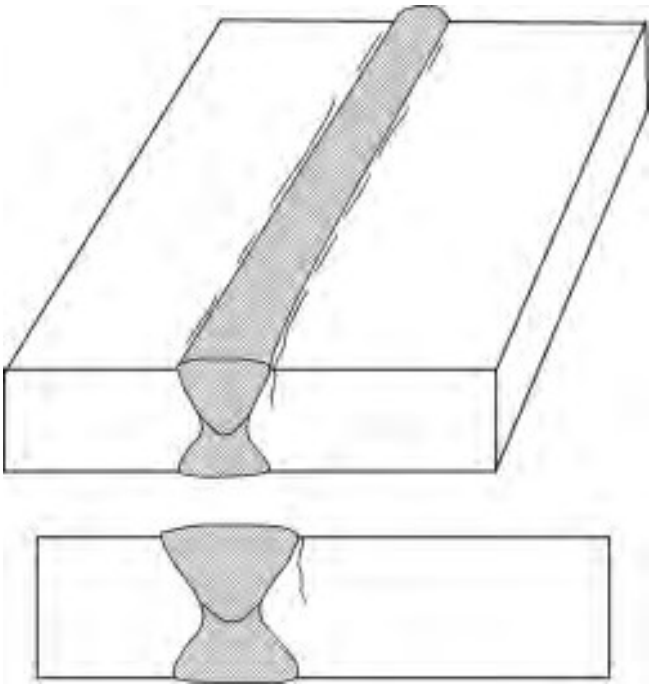

Figure 3-67-10—Illustration showing morphology of SSC in a hard HAZ.

4 Process Unit Process Flow Diagrams

Simplified process unit process flow diagrams (PFDs) for process units commonly found in many refineries are shown in this section. The PFDs are highlighted to show some of the areas within the unit where many of the primary damage mechanisms can be found. The reader should be advised that this is not intended to be an all-inclusive list of the damage mechanisms but should serve as a starting point for some of the major considerations.

The PFDs included in this section are listed below. A key to the Damage Mechanisms used on the PFDs is shown in Table 4-1.

— Crude Unit/Vacuum: Figure 4-1

— Delayed Coker: Figure 4-2

— Fluid Catalytic Cracking: Figure 4-3

— FCC Light Ends Recovery: Figure 4-4

— Catalytic Reforming—Continuous Catalytic Reforming (CCR): Figure 4-5

— Catalytic Reforming—Fixed Bed: Figure 4-6

— Hydroprocessing Units—Hydrotreating, Hydrocracking: Figure 4-7

— Sulfuric Acid Alkylation: Figure 4-8

— HF Alkylation: Figure 4-9

— Amine Treating: Figure 4-10

— Sulfur Recovery: Figure 4-11

— Sour Water Stripper: Figure 4-12

— Isomerization: Figure 4-13

— Hydrogen Reforming: Figure 4-14

— Visbreaker: Figure 4-15

— Caustic Treating: Figure 4-16

Table 4-1—Key to Damage Mechanisms

DM#	Damage Mechanism	DM#	Damage Mechanism
1	Sulfidation	36	Sulfuric Acid Corrosion
2	Wet H_2S Damage (Blistering/HIC/SOHIC/SSC)	37	Hydrofluoric Acid Corrosion
3	Creep and Stress Rupture	38	Flue Gas Dew Point Corrosion
4	High-temperature H_2/H_2S Corrosion	39	Dissimilar Metal Weld Cracking
5	Polythionic Acid Stress Corrosion Cracking	40	Hydrogen Stress Cracking in Hydrofluoric Acid
6	Naphthenic Acid Corrosion	41	Dealloying (Dezincification; Denickelification)
7	Ammonium Bisulfide Corrosion (Alkaline Sour Water)	42	CO_2 Corrosion
8	Ammonium Chloride Corrosion	43	Corrosion Fatigue
9	Hydrochloric Acid Corrosion	44	Fuel Ash Corrosion
10	High-temperature Hydrogen Attack	45	Amine Corrosion
11	Oxidation	46	Corrosion Under Insulation
12	Thermal Fatigue	47	Atmospheric Corrosion
13	Sour Water Corrosion (Acidic)	48	Ammonia Stress Corrosion Cracking
14	Refractory Degradation	49	Cooling Water Corrosion
15	Graphitization	50	Boiler Water and Condensate Corrosion
16	Temper Embrittlement	51	Microbiologically Influenced Corrosion
17	Decarburization	52	Liquid Metal Embrittlement
18	Caustic Stress Corrosion Cracking	53	Galvanic Corrosion
19	Caustic Corrosion	54	Mechanical Fatigue (Includes Vibration Fatigue)
20	Erosion/Erosion-Corrosion	55	Nitriding
21	Carbonate Stress Corrosion Cracking (ACSCC)	56	~~Vibration-Induced Fatigue~~ Withdrawn. See #54
22	Amine Stress Corrosion Cracking	57	Titanium Hydriding
23	Chloride Stress Corrosion Cracking	58	Soil Corrosion
24	Carburization	59	Metal Dusting
25	Hydrogen Embrittlement	60	Strain Aging
26	~~Steam Blanketing~~ Withdrawn. See #30.	61	~~Sulfate Stress Corrosion Cracking~~ Withdrawn
27	Thermal Shock	62	Phosphoric Acid Corrosion
28	Cavitation	63	Phenol (Carbolic Acid) Corrosion
29	Graphitic Corrosion of Cast Irons	64	Ethanol Stress Corrosion Cracking
30	Short-term Overheating—Stress Rupture (Including Steam Blanketing)	65	Gaseous Oxygen-enhanced Ignition and Combustion
31	Brittle Fracture	66	Aqueous Organic Acid Corrosion
32	Sigma Phase Embrittlement	67	Brine Corrosion
33	885 °F (475 °C) Embrittlement	68	Concentration Cell Corrosion
34	Spheroidization (Softening)	69	Hydrofluoric Acid Stress Corrosion Cracking of Nickel Alloys
35	Stress Relaxation Cracking (Reheat Cracking)	70	Oxygenated Water Corrosion (Non-boiler)

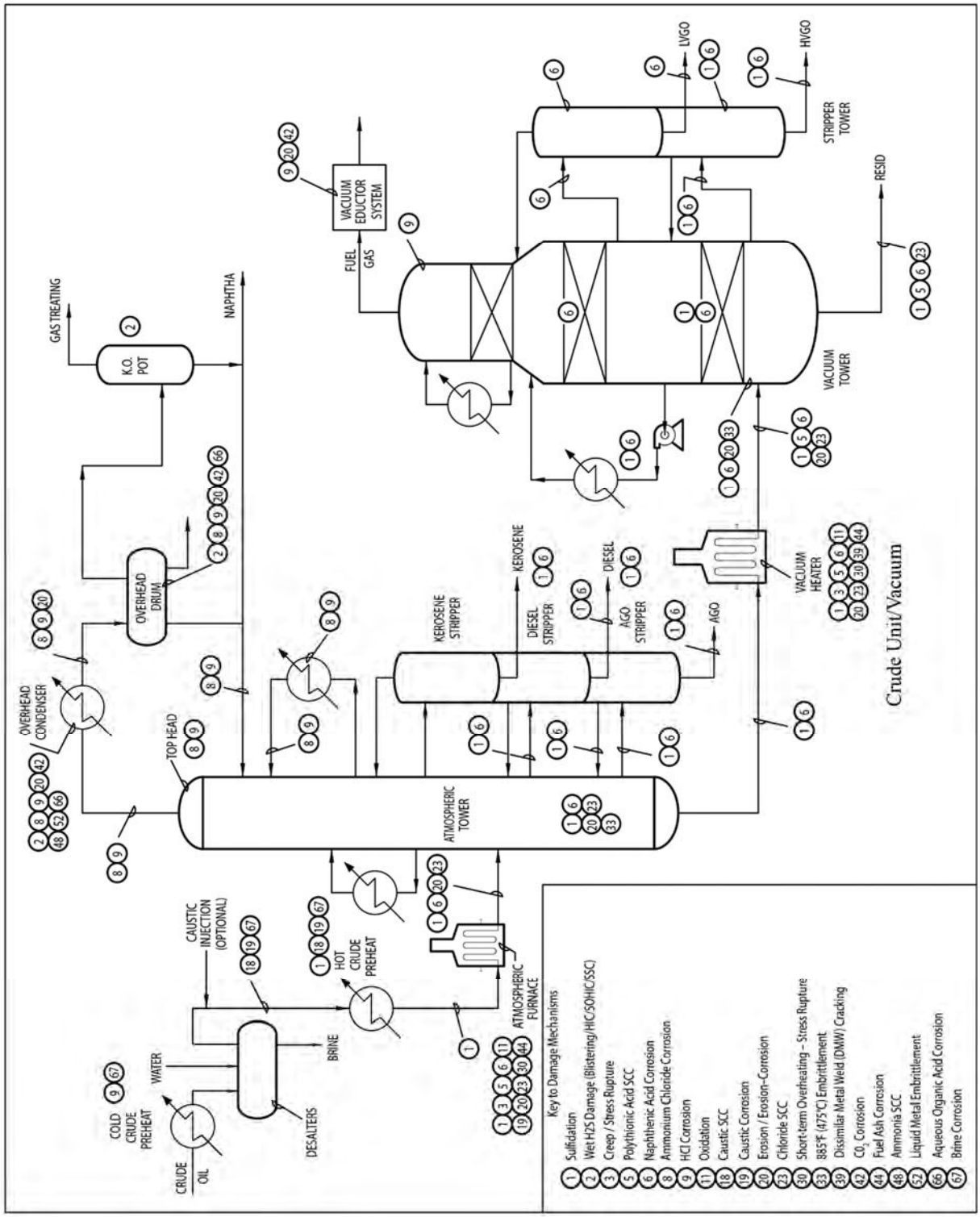

Figure 4-1—Crude Unit/Vacuum

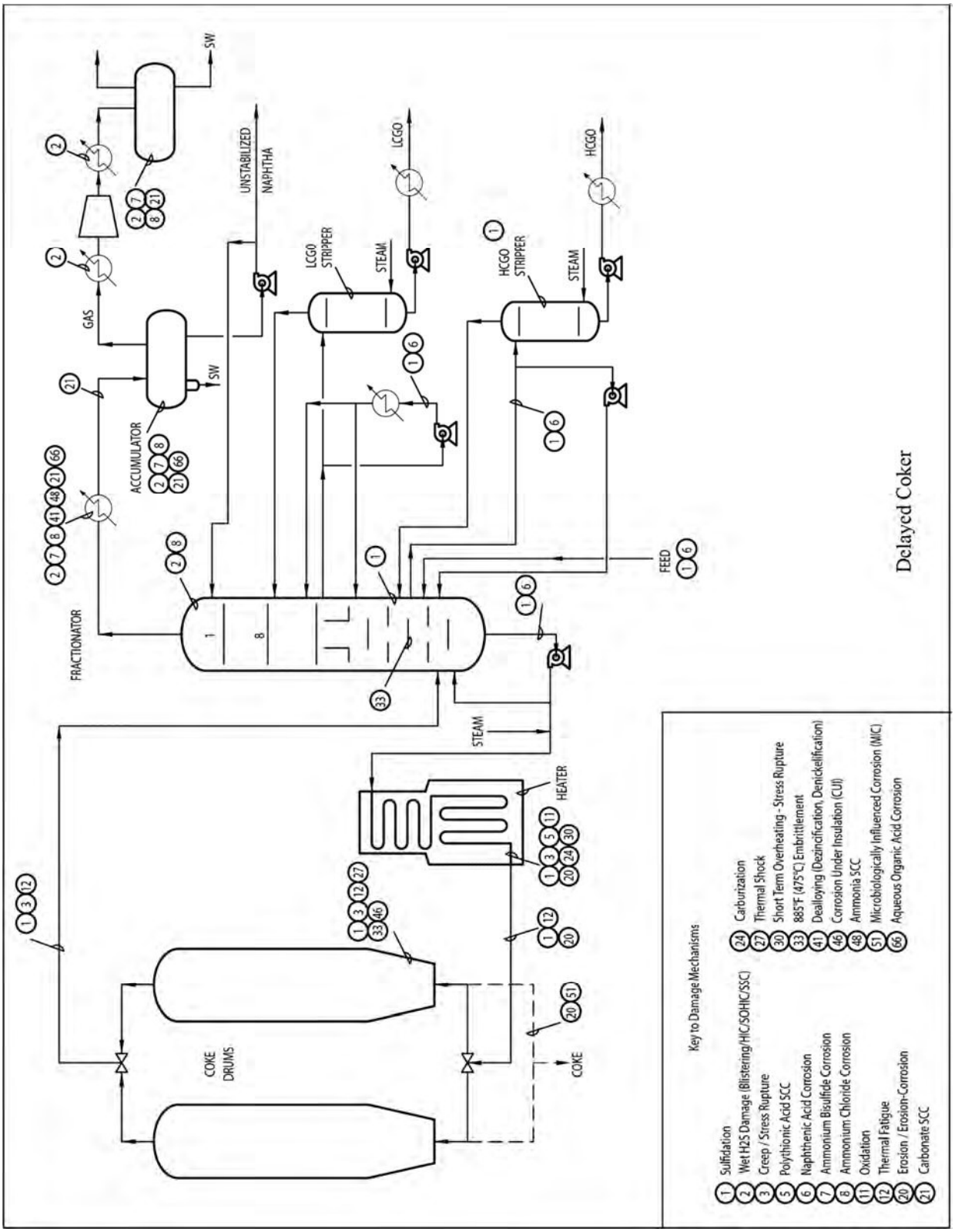

Figure 4-2—Delayed Coker

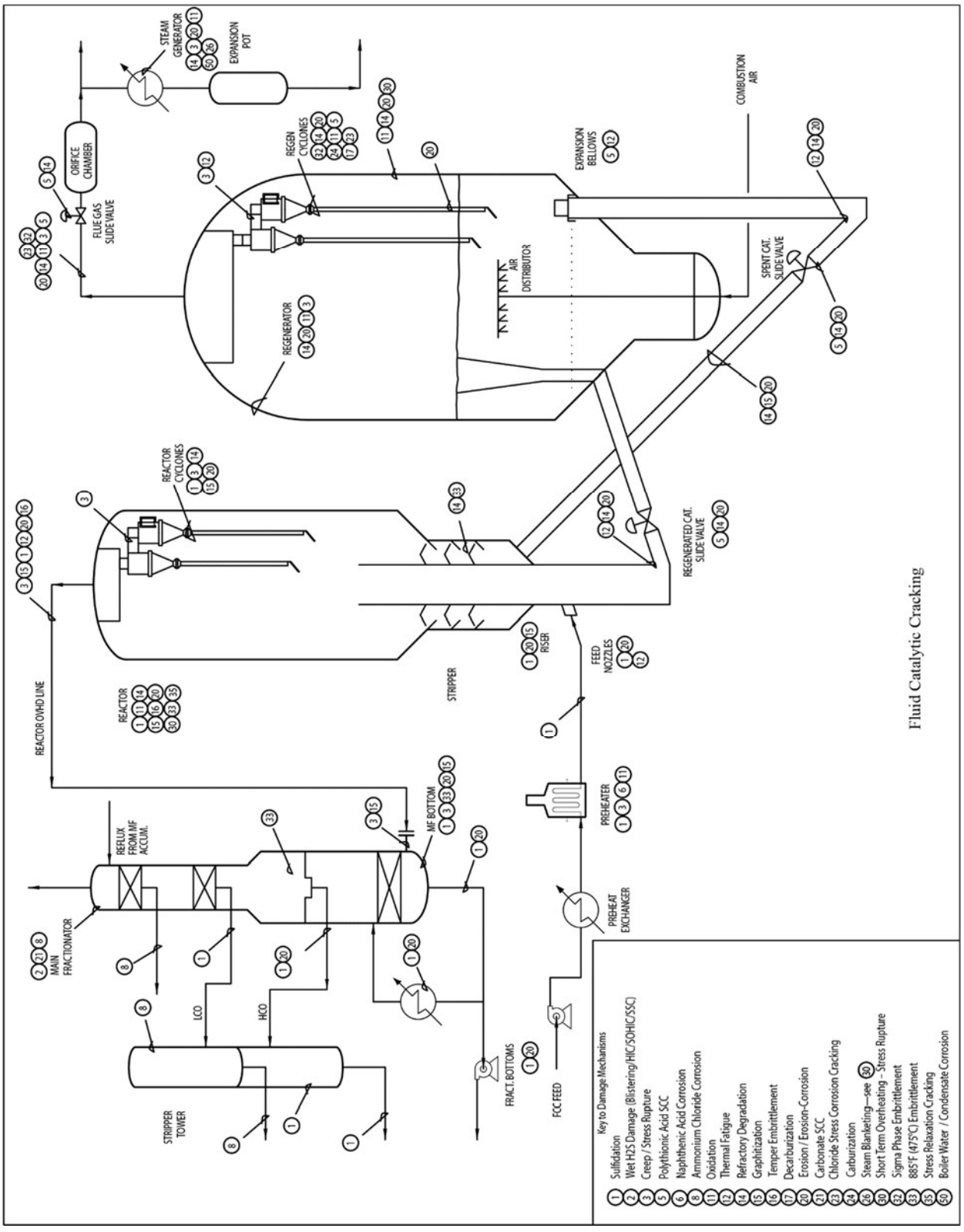

Figure 4-3—Fluid Catalytic Cracking

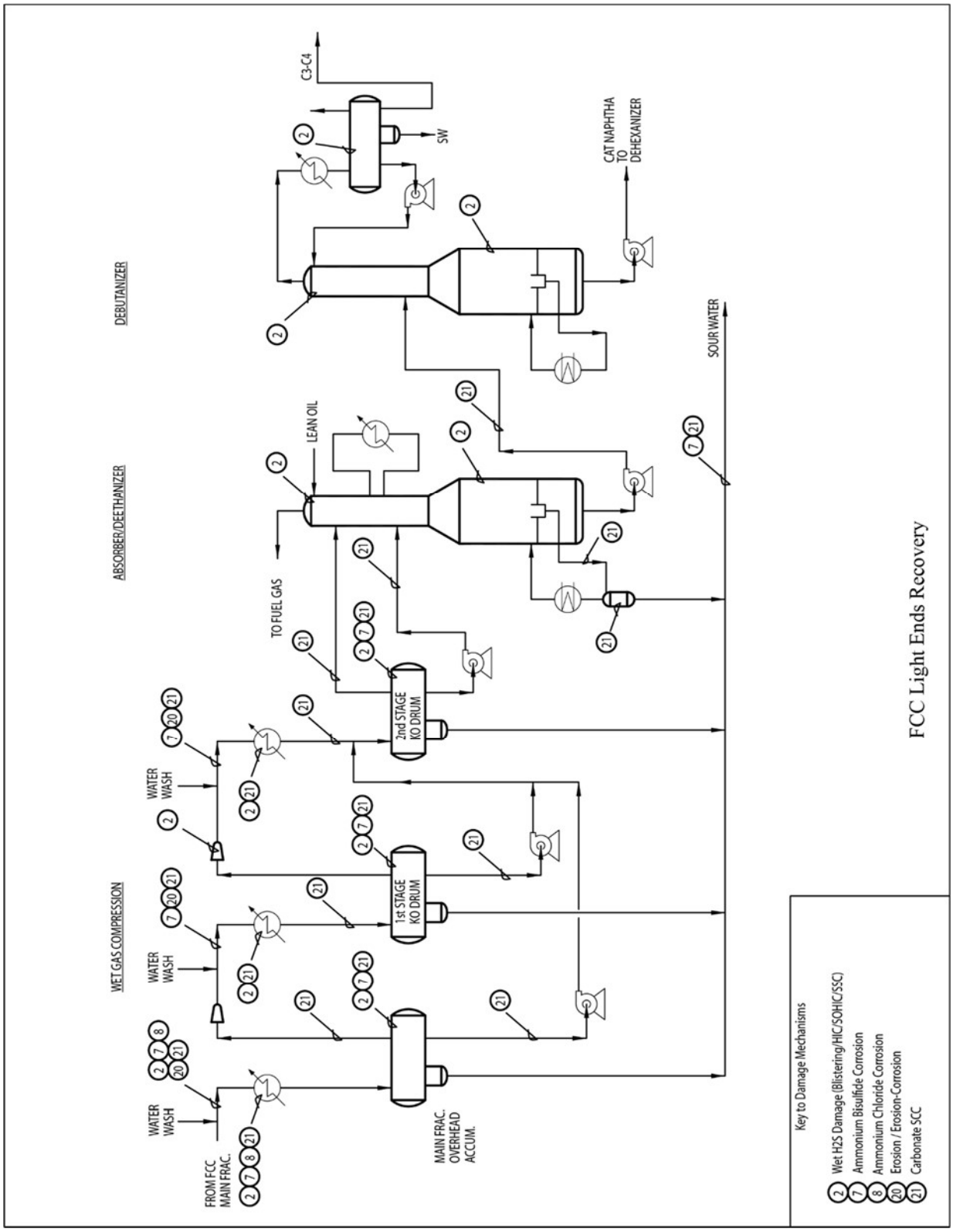

Figure 4-4—FCC Light Ends Recovery

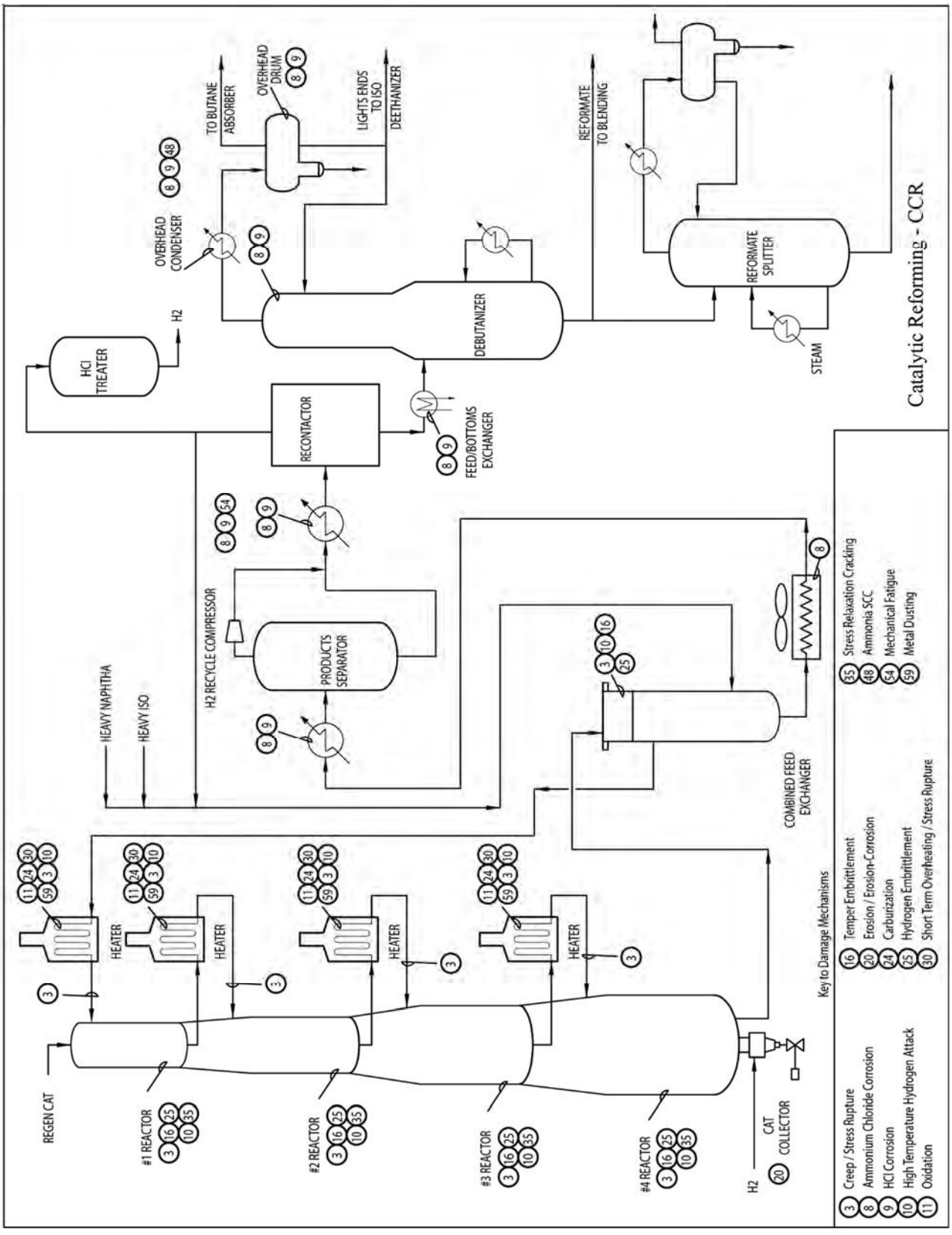

Figure 4-5—Catalytic Reforming—Continuous Catalytic Reforming (CCR)

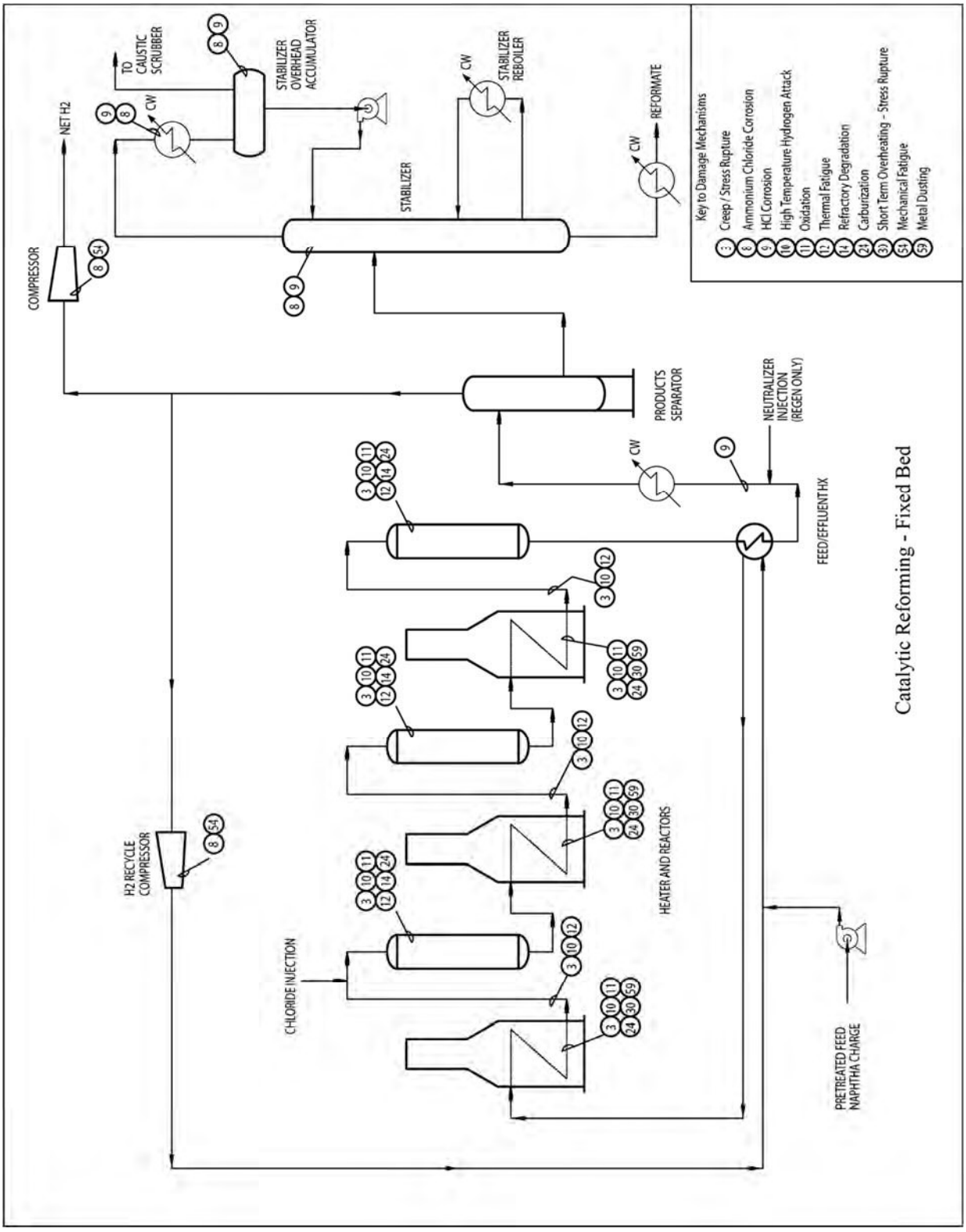

Figure 4-6—Catalytic Reforming—Fixed Bed

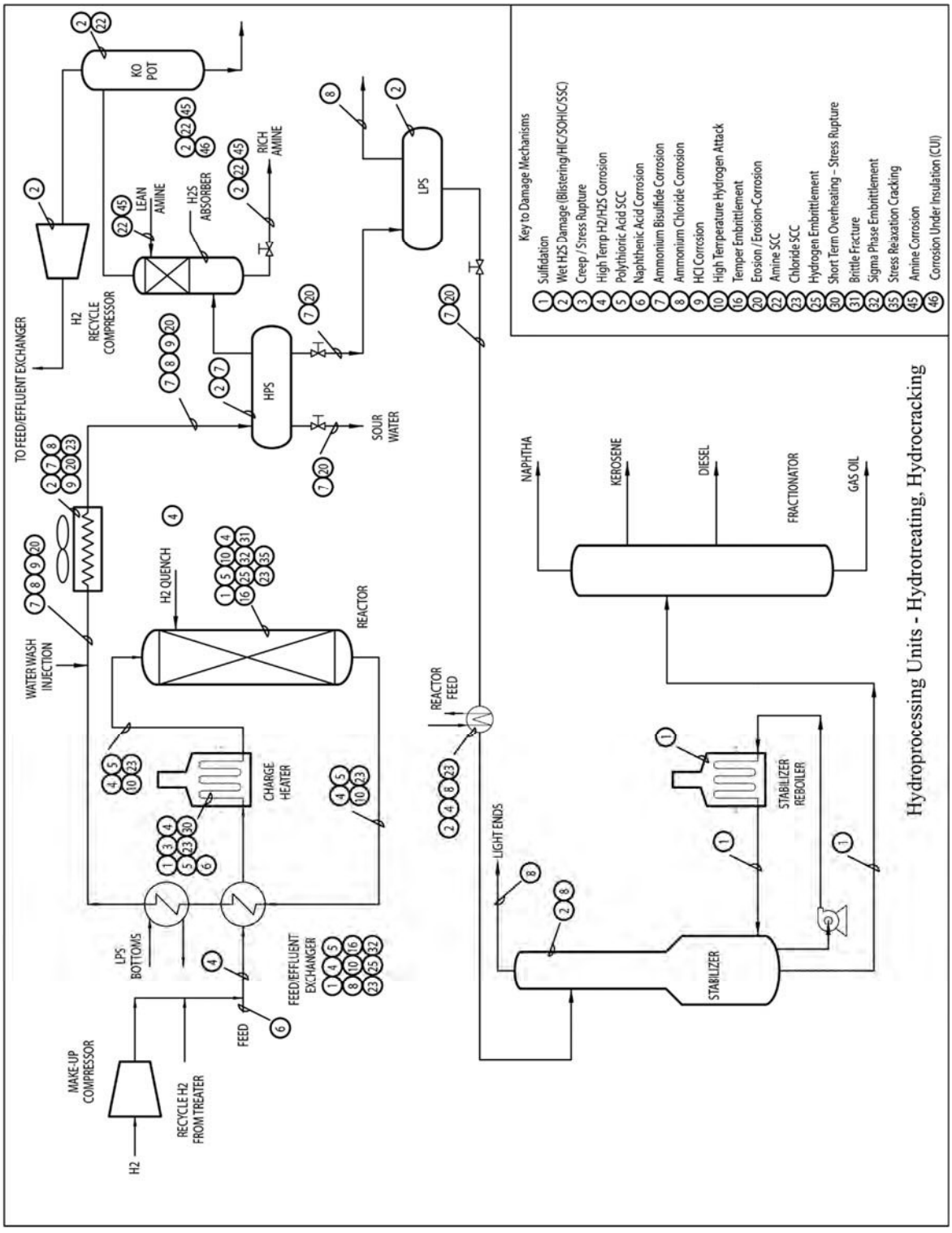

Figure 4-7—Hydroprocessing—Hydrotreating, Hydrocracking

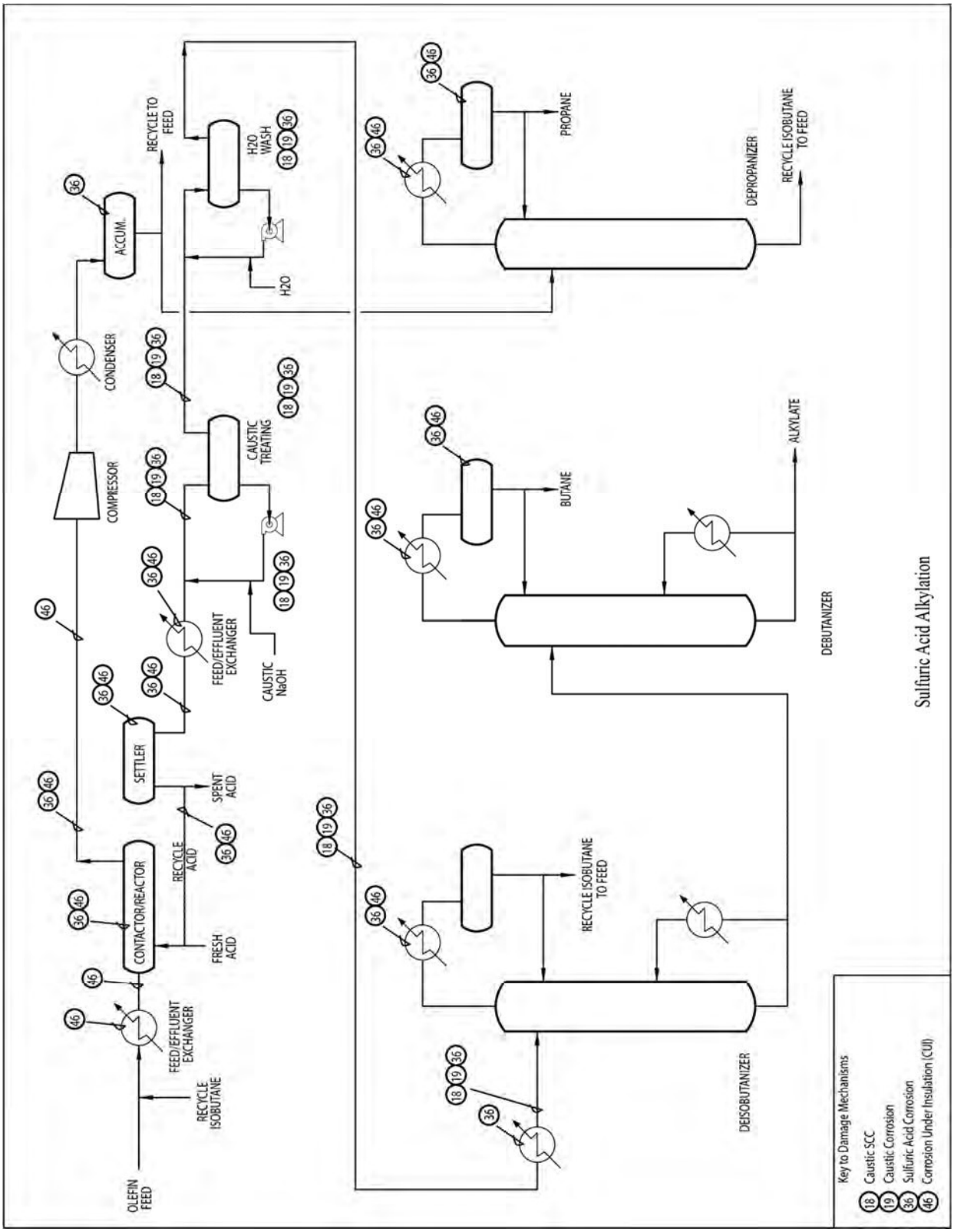

Figure 4-8—Sulfuric Acid Alkylation

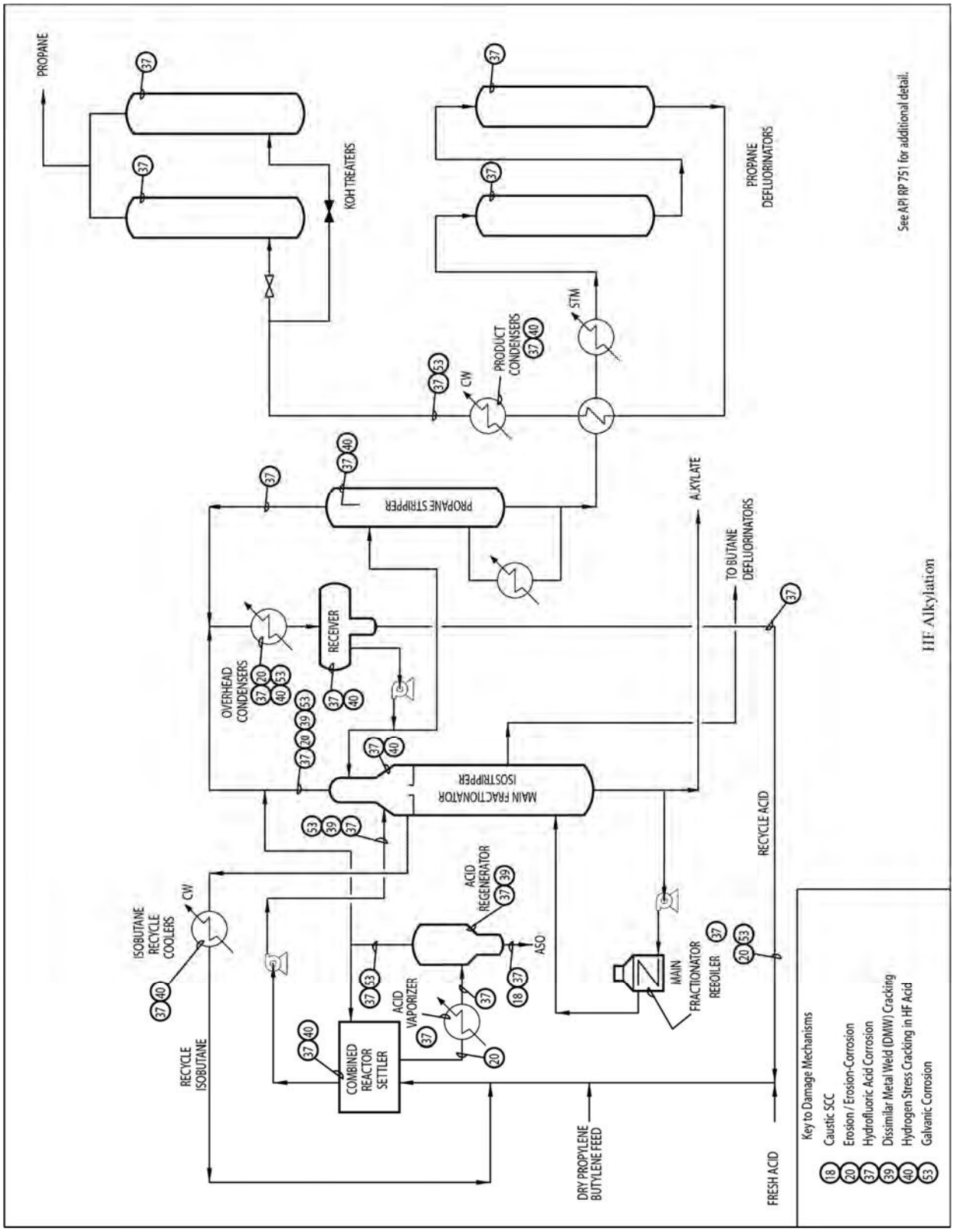

Figure 4-9—HF Alkylation

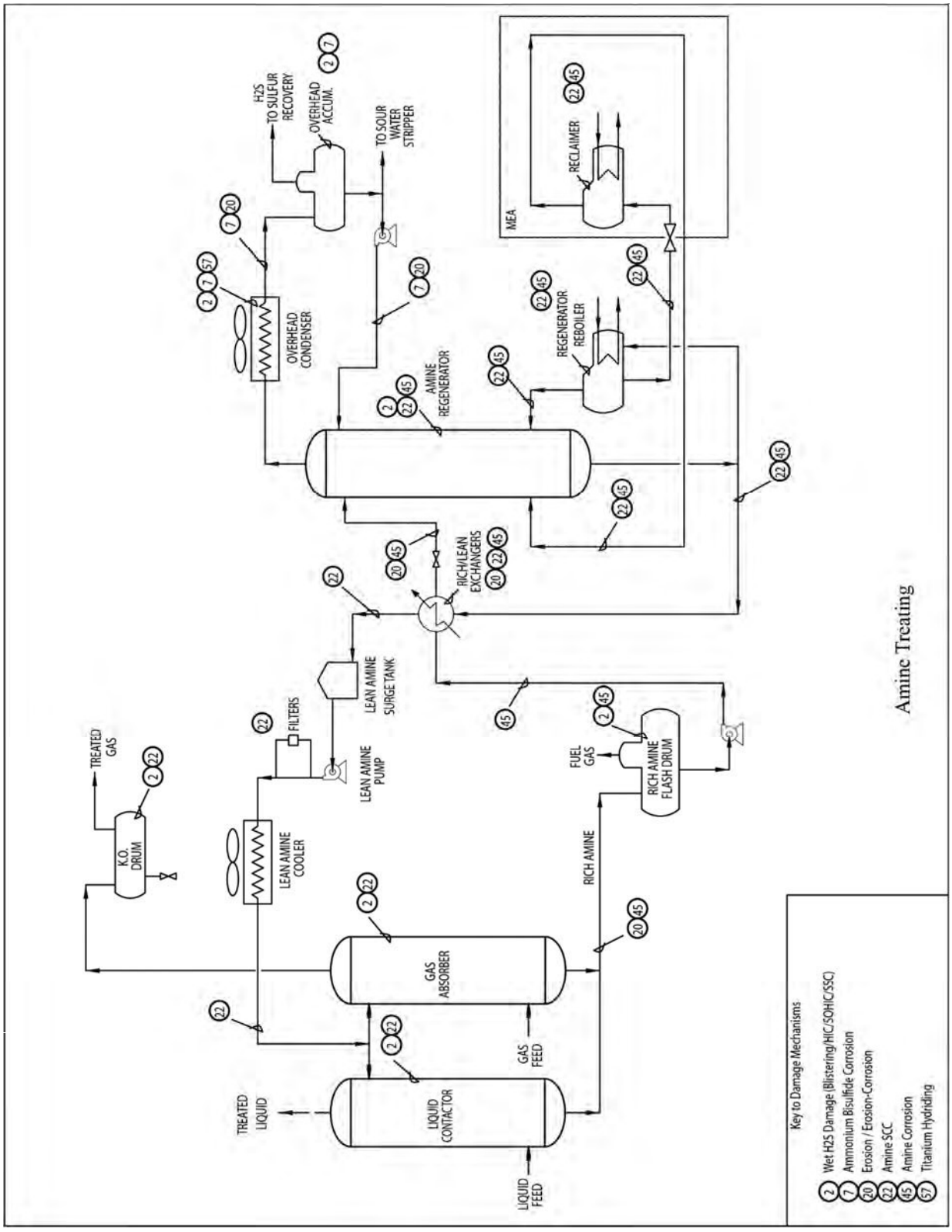

Figure 4-10—Amine Treating

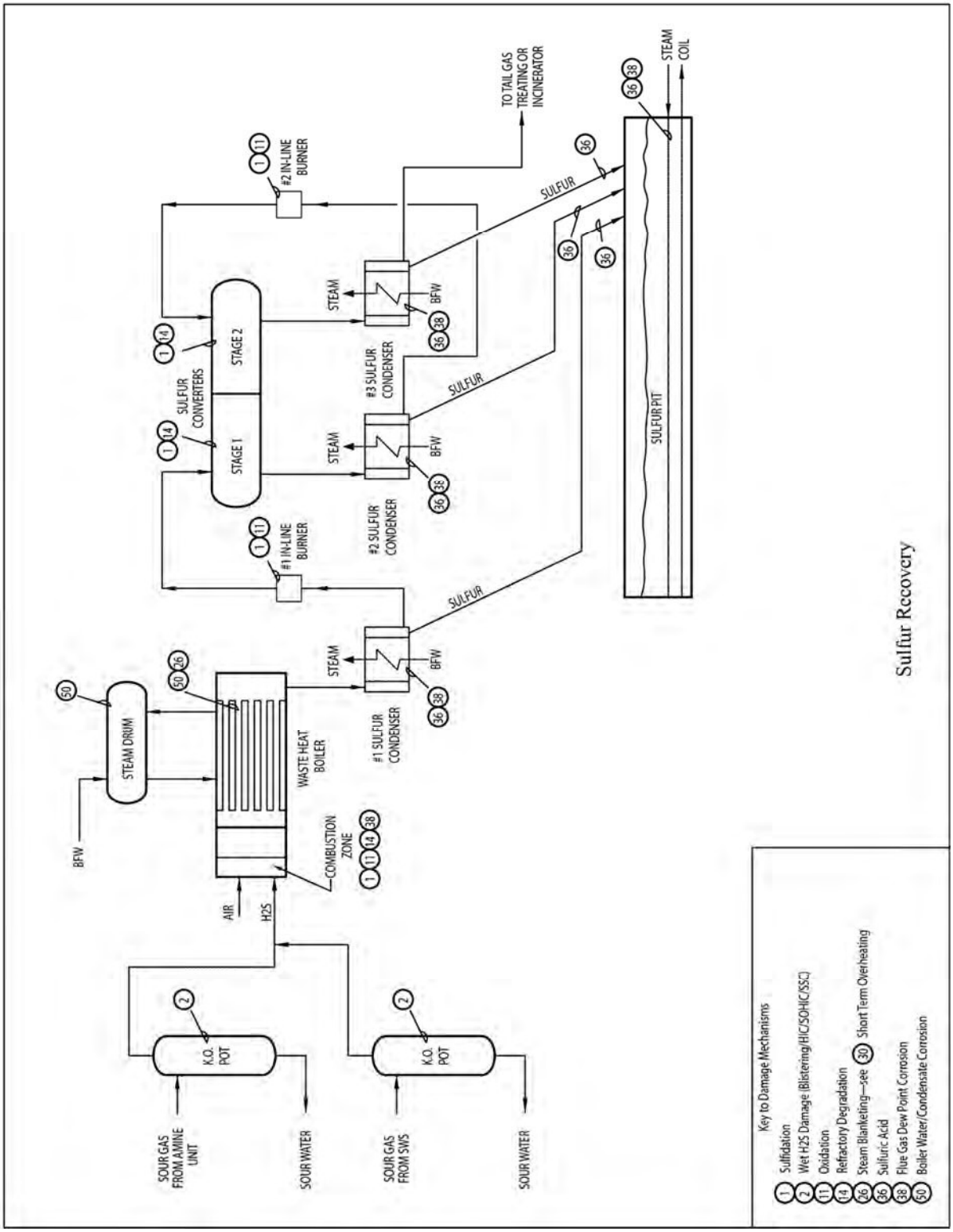

Figure 4-11—Sulfur Recovery

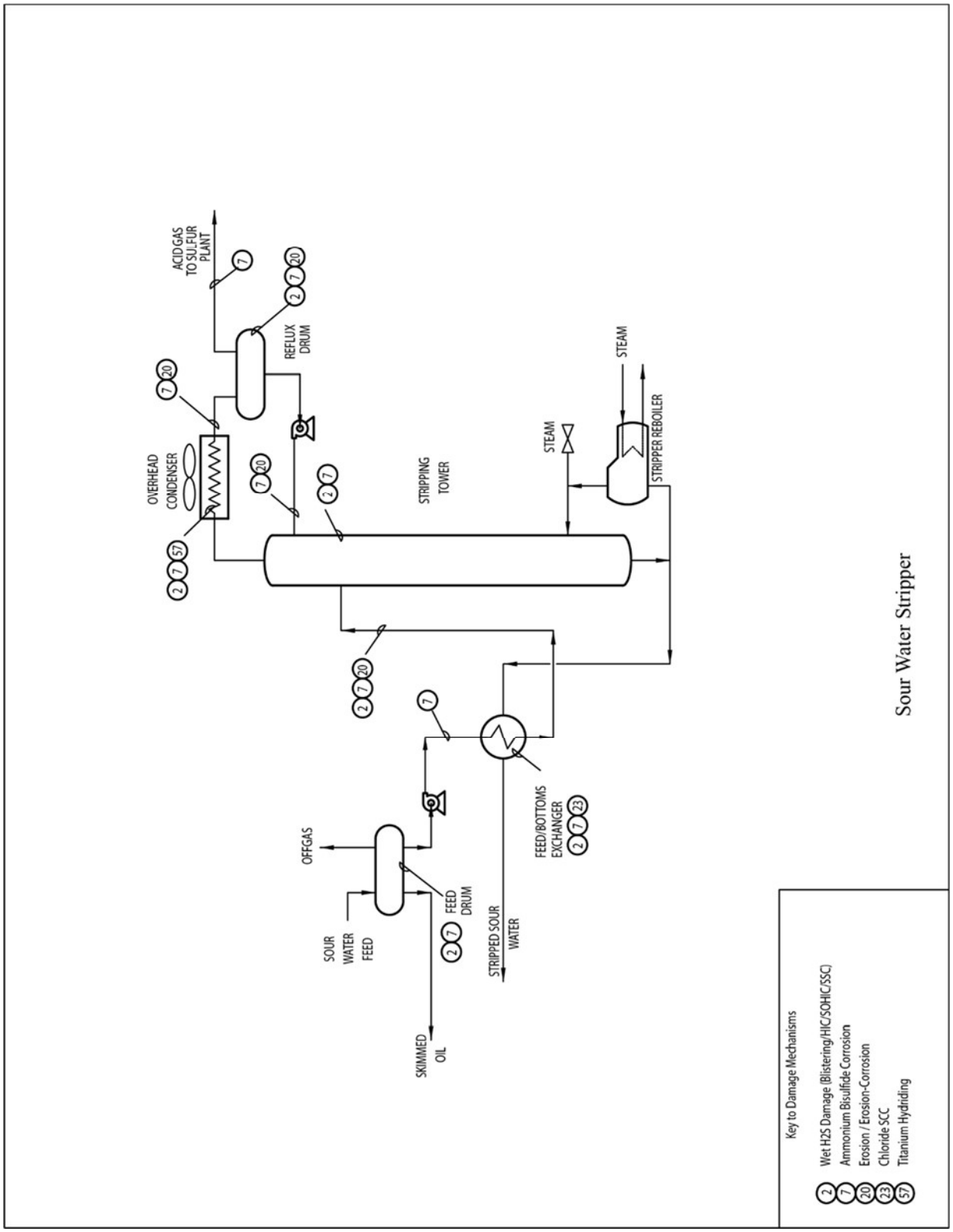

Figure 4-12—Sour Water Stripper

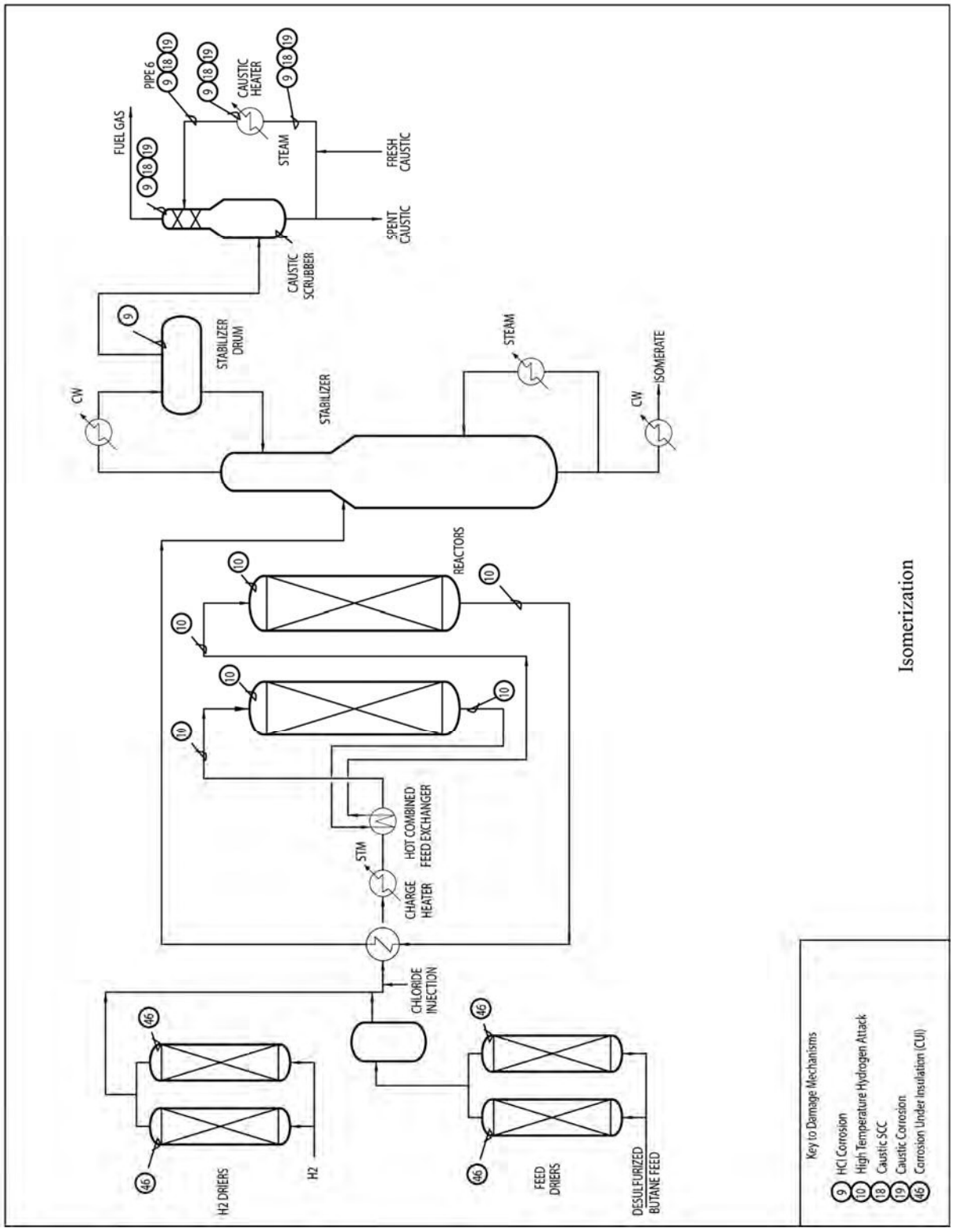

Figure 4-13—Isomerization

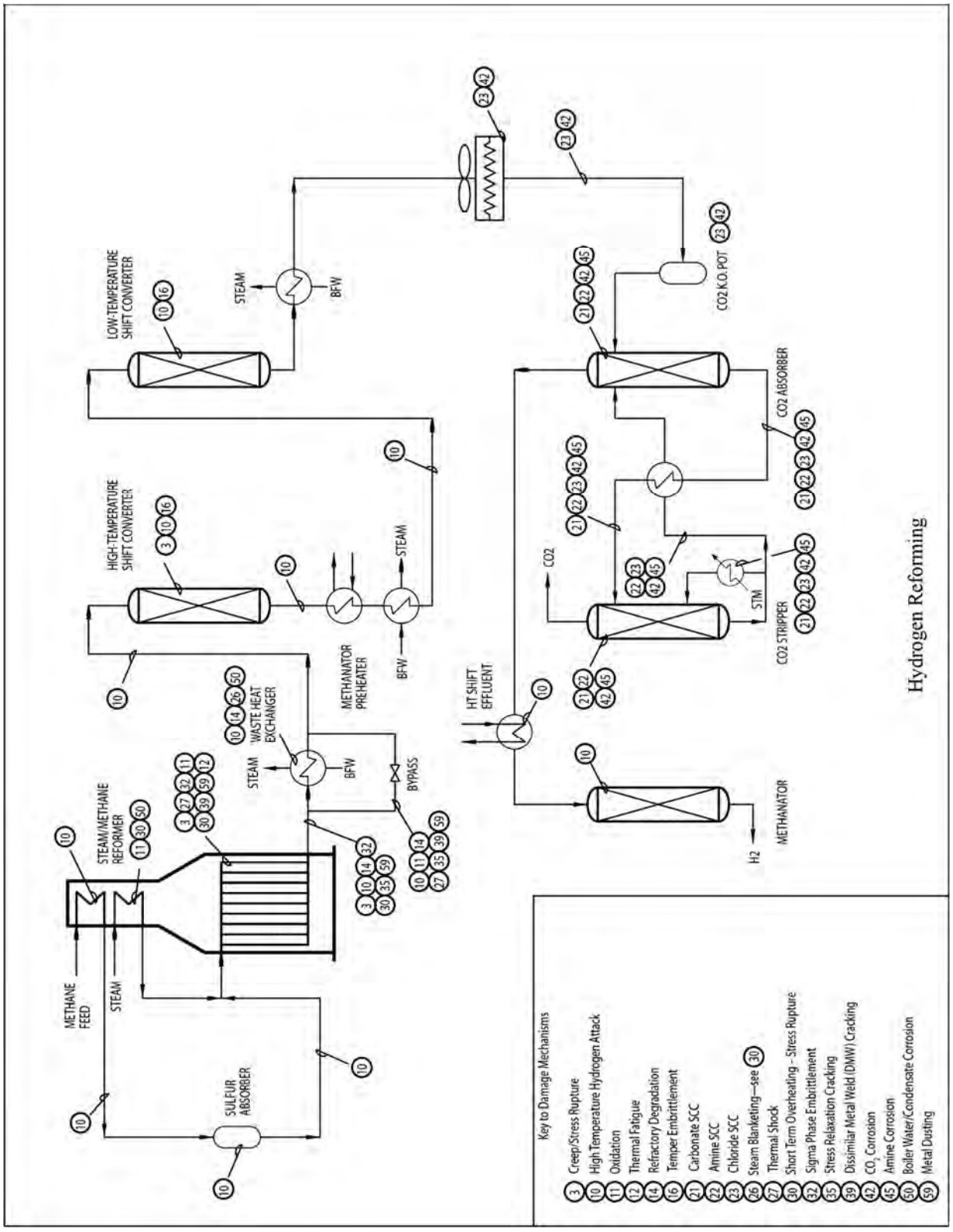

Figure 4-14—Hydrogen Reforming

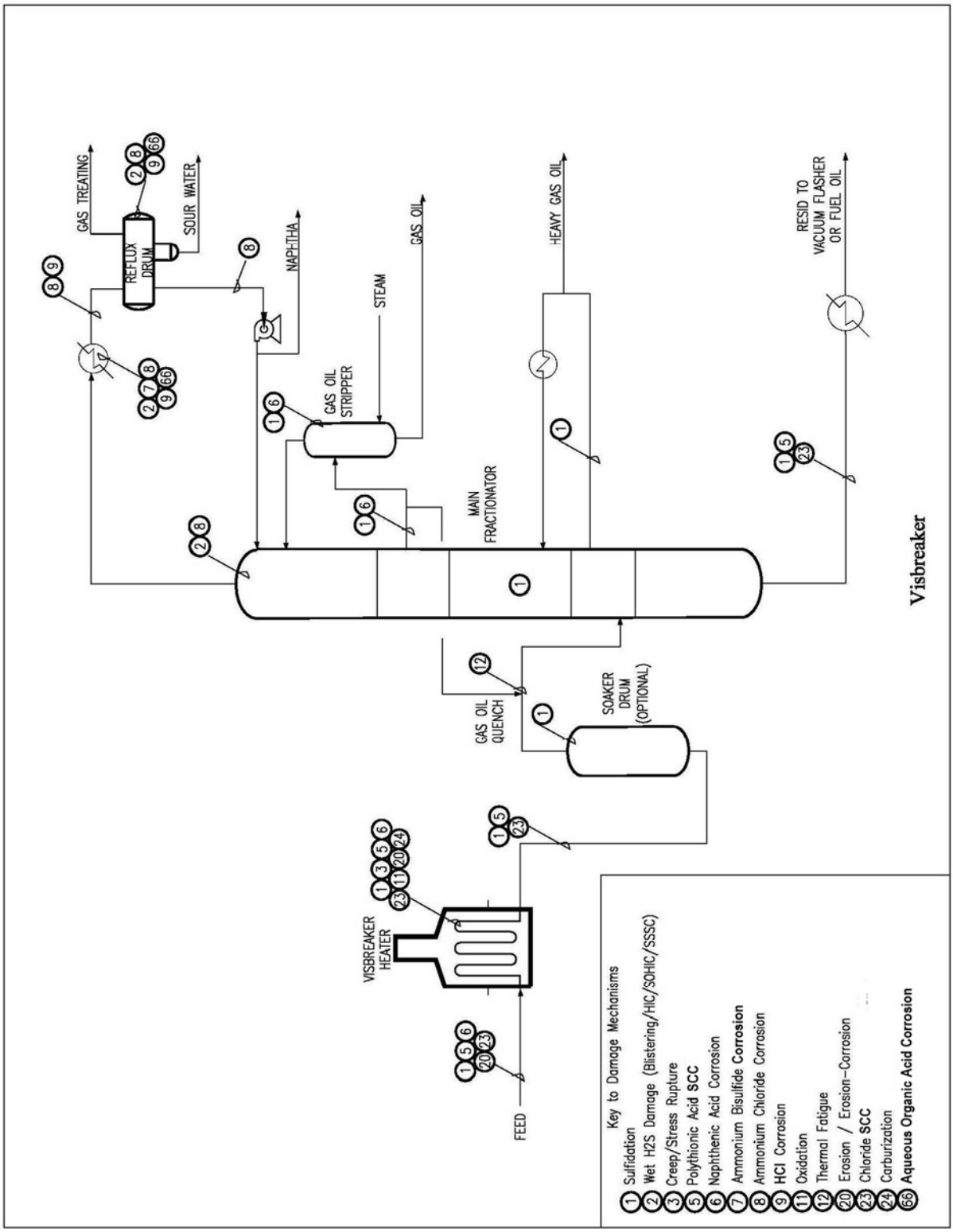

Figure 4-15—Visbreaker

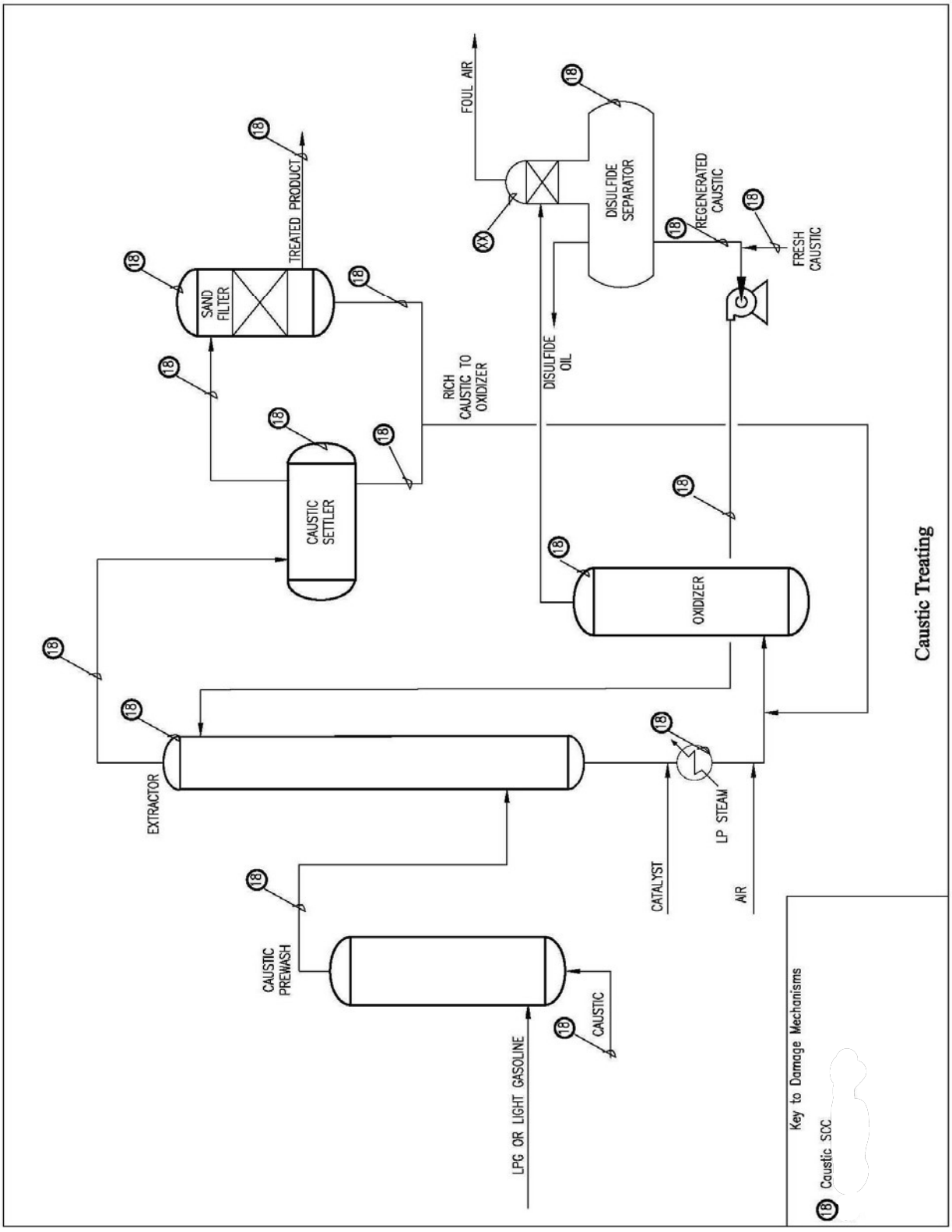

Figure 4-16—Caustic Treating

Annex A
(informative)

Useful Standards and References Relevant to this Recommended Practice

A.1 Codes and Standards

A.1.1 General

The following standards, codes, specifications, and other documents, some of which are cited in this recommended practice, provide useful information related to the subject matter of this recommended practice.

A.1.2 American Petroleum Institute Publications

API 510, *Pressure Vessel Inspection Code: In-service Inspection, Rating, Repair, and Alteration*

API Standard 530, *Calculation of Heater-tube Thickness in Petroleum Refineries*

API 570, *Piping Inspection Code: In-service Inspection, Repair, and Alteration of Piping Systems*

API Recommended Practice 572, *Inspection Practices for Pressure Vessels*

API Recommended Practice 573, *Inspection of Fired Boilers and Heaters*

API Recommended Practice 574, *Inspection Practices for Piping System Components*

API Recommended Practice 575, *Inspection Practices for Atmospheric and Low-pressure Storage Tanks*

API Recommended Practice 576, *Inspection of Pressure-relieving Devices*

API Recommended Practice 577, *Welding Inspection and Metallurgy*

API Recommended Practice 578, *Guidelines for a Material Verification Program (MVP) for New and Existing Assets*

API Recommended Practice 580, *Risk-Based Inspection*

API Recommended Practice 581, *Risk-Based Inspection Methodology*

API Recommended Practice 582, *Welding Guidelines for the Chemical, Oil, and Gas Industries*

API Recommended Practice 583, *Corrosion Under Insulation and Fireproofing*

API Recommended Practice 584, *Integrity Operating Windows*

API Recommended Practice 585, *Pressure Equipment Integrity Incident Investigation*

API 579-1/ASME FFS-1, *Fitness-For-Service*

API Standard 653, *Tank Inspection, Repair, Alteration, and Reconstruction*

API Standard 660, *Shell-and-Tube Heat Exchangers*

API Recommended Practice 751, *Safe Operation of Hydrofluoric Acid Alkylation Units*

API Technical Report 932-A, *A Study of Corrosion in Hydroprocess Reactor Effluent Air Cooler Systems*

API Recommended Practice 932-B, *Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems*

API Recommended Practice 934-A, *Materials and Fabrication of 2¼Cr-1Mo, 2¼Cr-1Mo-¼V, 3Cr-1Mo, and 3Cr-1Mo-¼V Steel Heavy Wall Pressure Vessels for High-temperature, High-pressure Hydrogen Service*

API Technical Report 934-B, *Fabrication Considerations for Vanadium-Modified Cr-Mo Steel Heavy Wall Pressure Vessels*

API Recommended Practice 934-C, *Materials and Fabrication of 1¼Cr-½Mo Steel Heavy Wall Pressure Vessels for High-pressure Hydrogen Service Operating at or Below 825 °F (441 °C)*

API Technical Report 934-D, *Technical Report on the Materials and Fabrication Issues of 1¼Cr-½Mo and 1Cr-½Mo Steel Pressure Vessels*

API Recommended Practice 934-E, *Recommended Practice for Materials and Fabrication of 1¼Cr-½Mo Steel Pressure Vessels for Service Above 825 °F (440 °C)*

API Technical Report 934-G, *Design, Fabrication, Operational Effects, Inspection, Assessment, and Repair of Coke Drums and Peripheral Components in Delayed Coking Units*

API Publication 938-A, *Experimental Study of Causes and Repair of Cracking of 1¼Cr-½Mo Steel Equipment*

API Publication 938-B, *Use of 9Cr-1Mo-V (Grade 91) Steel in the Oil Refining Industry*

API Technical Report 938-C, *Use of Duplex Stainless Steels in the Oil Refining Industry*

API Technical Report 939-A, *Research Report on Characterization and Monitoring of Cracking in Wet H_2S Service*

API Technical Report 939-B, *Repair and Remediation Strategies for Equipment Operating in Wet H_2S Service*

API Recommended Practice 939-C, *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries*

API Technical Report 939-D, *Stress Corrosion Cracking of Carbon Steel in Fuel-grade Ethanol: Review, Experience Survey, Field Monitoring, and Laboratory Testing*

API Bulletin 939-E*, Identification, Repair, and Mitigation of Cracking of Steel Equipment in Fuel Ethanol Service*

API Recommended Practice 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*

API Technical Report 941, *The Technical Basis Document for API RP 941*

API Technical Report 942-A, *Materials, Fabrication, and Repair Considerations for Hydrogen Reformer Furnace Outlet Pigtails and Manifolds*

API Technical Report 942-B, *Material, Fabrication, and Repair Considerations for Austenitic Alloys Subject to Embrittlement and Cracking in High Temperature 565 °C to 760 °C (1050 °F to 1400 °F) Refinery Services*

API Recommended Practice 945, *Avoiding Environmental Cracking in Amine Units*

A.1.3 Other Publications

ASM Handbook [1], Volume 1—*Properties and Selection: Iron, Steels, and High-performance Alloys*; Volume 11—*Failure Analysis and Prevention*; Volume 13—*Corrosion*

ASME *Boiler and Pressure Vessel Code* (*BPVC*) [2], *Section VIII: Rules for Construction of Pressure Vessels; Divisions 1 & 2*

ASTM MNL41 [3], *Fracture and Fatigue Control in Structures: Applications of Fracture Mechanics*

ASTM STP1428, *Thermomechanical Fatigue Behavior of Materials*

BS 7910 [4], *Guide to Methods for Assessing the Acceptability of Flaws in Metallic Structures*

MPC Report FS-26 [5], *Fitness-For Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service*

NACE MR0103 [6]/ISO 17945 [7], *Petroleum, petrochemical and natural gas industries—Metallic materials resistant to sulfide stress cracking in corrosive petroleum refining environments*

NACE Publication 5A151, *Materials of Construction for Handling Sulfuric Acid*

NACE Publication 5A171, *Materials for Storing and Handling Commercial Grades of Aqueous Hydrofluoric Acid and Anhydrous Hydrogen Fluoride*

NACE Publication 8X194, *Materials and Fabrication Practices for New Pressure Vessels Used in Wet H_2S Refinery Service*

NACE Publication 34105, *Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling*

NACE Publication 34108, *Review and Survey of Alkaline Carbonate Stress Corrosion Cracking in Refinery Sour Waters*

NACE SP0169, *Control of External Corrosion on Underground or Submerged Metallic Piping Systems*

NACE SP0170, *Protection of Austenitic Stainless Steels and Other Austenitic Alloys from Polythionic Acid Stress Corrosion Cracking During a Shutdown of Refinery Equipment*

NACE SP0198, *Control of Corrosion Under Thermal Insulation and Fireproofing Materials—A Systems Approach*

NACE SP0294, *Design, Fabrication, and Inspection of Storage Tank Systems for Concentrated Fresh and Process Sulfuric Acid and Oleum at Ambient Temperatures*

NACE SP0296, *Detection, Repair, and Mitigation of Cracking in Refinery Equipment in Wet H_2S Environments*

NACE SP0403, *Avoiding Caustic Stress Corrosion Cracking of Refinery Equipment and Piping*

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[1] ASM International, 9639 Kinsman Road, Materials Park, OH 44073-0002, www.asminternational.org.

[2] ASME International, 2 Park Avenue, New York, NY 10016-5990, www.asme.org.

[3] ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, www. astm.org.

[4] British Standard Institution, 389 Chiswick High Road, London W4 4AL, UK, www.bsi-global.com.

[5] Materials Properties Council (part of the Welding Research Council), P.O. Box 201547, Shaker Heights, OH 44122, www.forengineers.org/mpc.

[6] NACE International, 15835 Park Ten Place, Houston, TX 77084, www.nace.org.

[7] International Organization for Standardization, 1, ch. de la Voie-Creuse, Case postale 56, CH-1211 Geneva 20, Switzerland, www.iso.org.

NACE SP0472, *Methods and Controls to Prevent In-service Environmental Cracking of Carbon Steel Weldments in Corrosive Petroleum Refining Environments*

NACE SP0590, *Prevention, Detection, and Correction of Deaerator Cracking*

WRC Bulletin 032 [8], *Part 1: Graphitization of Steel in Petroleum Refining Equipment*

WRC Bulletin 275, *The Use of Quenched and Tempered 2¼Cr-1Mo Steel for Thick Wall Reactor Vessels in Petroleum Refinery Processes: An Interpretive Review of 25 Years of Research and Application*

WRC Bulletin 350, *Design Criteria for Dissimilar Metal Welds*

WRC Bulletin 409, *Fundamental Studies of the Metallurgical Causes and Mitigation of Reheat Cracking* in *1¼Cr-½Mo and 2¼Cr-1Mo Steels*

WRC Bulletin 418, *Part 1: Constraint Effects on Fracture Behavior: The Effect of Crack Depth (a) and Crack-depth to Width Ratio (a/W) on the Fracture Toughness of A533-B Steel*

WRC Bulletin 452, *Recommended Practices for Local Heating of Welds in Pressure Vessels*

[8] Welding Research Council, P.O. Box 201547, Shaker Heights, OH 44122, www.forengineers.org/wrc.

Annex B
(informative)

Technical Inquiries

B.1 Introduction

API will consider written requests for interpretations of API 571. The API staff will make such interpretations in writing after consulting, if necessary, with the appropriate committee officers and committee members. The API committee responsible for maintaining API 571 meets regularly to consider written requests for interpretations and revisions and to develop new criteria dictated by technological development. The committee's activities in this regard are limited strictly to interpretations of the document and to the consideration of revisions to the current edition of the document on the basis of new data or technology. As a matter of policy, API does not approve, certify, rate, or endorse any item, construction, proprietary device, or activity, and, accordingly, inquiries that require such consideration will be returned. Moreover, API does not act as a consultant on specific engineering problems or on the general understanding or application of API 571. If, based on the inquiry information submitted, it is the opinion of the committee that the inquirer should seek other assistance, the inquiry will be returned with the recommendation that such assistance be obtained. All inquiries that cannot be understood because they lack information will be returned.

B.2 Inquiry Format

B.2.1 Inquiries shall be limited strictly to requests for interpretation of API 571 or to the consideration of revisions to the document on the basis of new data or technology. Inquiries shall be submitted in the format described in B.2.2.

B.2.2 The process for submitting a technical inquiry is explained in detail on the API website at: http://rfi.api.org/. Please read the information on this page for any updates to the process. You may also access an online form for submitting your request.

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