Damage Mechanisms Affecting Fixed Equipment in the Refining Industry

ANSI/API RECOMMENDED PRACTICE 571
THIRD EDITION, MARCH 2020

Special Notes

API publications necessarily address problems of a general nature. With respect to particular circumstances, local, state, and federal laws and regulations should be reviewed.

Neither API nor any of API's employees, subcontractors, consultants, committees, or other assignees make any warranty or representation, either express or implied, with respect to the accuracy, completeness, or usefulness of the information contained herein, or assume any liability or responsibility for any use, or the results of such use, of any information or process disclosed in this publication. Neither API nor any of API's employees, subcontractors, consultants, or other assignees represent that use of this publication would not infringe upon privately owned rights.

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to assure the accuracy and reliability of the data contained in them; however, the Institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any authorities having jurisdiction with which this publication may conflict.

API publications are published to facilitate the broad availability of proven, sound engineering and operating practices. These publications are not intended to obviate the need for applying sound engineering judgment regarding when and where these publications should be utilized. The formulation and publication of API publications is not intended in any way to inhibit anyone from using any other practices.

Any manufacturer marking equipment or materials in conformance with the marking requirements of an API standard is solely responsible for complying with all the applicable requirements of that standard. API does not represent, warrant, or guarantee that such products do in fact conform to the applicable API standard.

Classified areas may vary depending on the location, conditions, equipment, and substances involved in any given situation. Users of this recommended practice should consult with the appropriate authorities having jurisdiction.

Users of this recommended practice should not rely exclusively on the information contained in this document. Sound business, scientific, engineering, and safety judgment should be used in employing the information contained herein.

Information concerning safety and health risks and proper precautions with respect to particular materials and conditions should be obtained from the employer, the manufacturer or supplier of that material, or the material safety data sheet.

API is not undertaking to meet the duties of employers, manufacturers, or suppliers to warn and properly train and equip their employees, and others exposed, concerning health and safety risks and precautions, nor undertaking their obligations to comply with authorities having jurisdiction.

Where applicable, authorities having jurisdiction should be consulted.

Work sites and equipment operations may differ. Users are solely responsible for assessing their specific equipment and premises in determining the appropriateness of applying the recommended practice. At all times users should employ sound business, scientific, engineering, and judgment safety when using this recommended practice.

Foreword

Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

The verbal forms used to express the provisions in this document are as follows.

Shall: As used in a standard, “shall” denotes a minimum requirement in order to conform to the standard.

Should: As used in a standard, “should” denotes a recommendation or that which is advised but not required in order to conform to the standard.

May: As used in a standard, “may” denotes a course of action permissible within the limits of a standard.

Can: As used in a standard, “can” denotes a statement of possibility or capability.

This document was produced under API standardization procedures that ensure appropriate notification and participation in the developmental process and is designated as an API standard. Questions concerning the interpretation of the content of this publication or comments and questions concerning the procedures under which this publication was developed should be directed in writing to the Director of Standards, American Petroleum Institute, 200 Massachusetts Avenue, NW, Suite 1100, Washington, DC 20001. Requests for permission to reproduce or translate all or any part of the material published herein should also be addressed to the director.

Generally, API standards are reviewed and revised, reaffirmed, or withdrawn at least every five years. A one-time extension of up to two years may be added to this review cycle. Status of the publication can be ascertained from the API Standards Department, telephone (202) 682-8000. A catalog of API publications and materials is published annually by API, 200 Massachusetts Avenue, NW, Suite 1100, Washington, DC 20001.

Suggested revisions are invited and should be submitted to the Standards Department, API, 200 Massachusetts Avenue, NW, Suite 1100, Washington, DC 20001, standards@api.org.

Contents

Contents

Introduction

While ASME and API design codes and standards provide rules for the design, fabrication, inspection, and testing of new pressure vessels, piping systems, and storage tanks, they do not address equipment deterioration while in service, nor do they account for original fabrication defects not discovered during construction but found during subsequent inspections.

The interactions between the materials of construction and the environmental conditions to which they are exposed, including process conditions and external conditions, are extremely varied within an operating oil refinery. Oil refineries contain many different processing units, each having its own combination of process streams and temperature/pressure conditions. The purpose of this recommended practice is to describe the wide variety of service-induced damage and deterioration mechanisms, including corrosion and other types of metallurgical damage, that are most likely to affect the condition of the materials of construction commonly used in refinery equipment.

This document incorporates information gathered from major incidents in the refining industry and is intended to be consistent with applicable API documents as well as other related industry standards and practices. It is meant to provide guidance to pressure equipment integrity personnel but should not be considered the final technical basis for damage mechanism assessment and analysis or inspection and monitoring. The damage mechanism descriptions herein are not intended to provide a definitive guideline for every possible situation that may be encountered, and the reader may need to consult with an engineer or other corrosion specialist familiar with applicable degradation modes and failure mechanisms, particularly those that apply in special cases.

Damage Mechanisms Affecting Fixed Equipment in the Refining Industry

1 Scope

This recommended practice discusses damage mechanisms applicable to oil refineries; however, much of the information herein can also be applied to petrochemical and other industrial applications, as the user deems appropriate. It is up to the user to determine the applicability and appropriateness of the information contained herein as it applies to their facility.

API 571 is a reference document that provides useful information by itself and also complements other API standards and recommended practices. The document should be utilized as a reference to other integrity related documents. It is intended to contribute to the overall management of pressure equipment integrity and is a useful resource for many mechanical integrity program activities including:

a) identification of existing damage or deterioration and anticipated rates of degradation,

b) identification of future damage mechanism susceptibilities,

c) development and maintenance of inspection and monitoring strategies, programs, and plans (e.g. per API 510, API 570, and API 653),

d) implementation and monitoring of integrity operating windows (IOWs) (see API 584),

e) development of corrosion control documents (CCDs) (see API 970),

f) implementation of Risk-Based Inspection (RBI) programs (see API 580 and API 581),

g) conducting Fitness-For-Service (FFS) assessments (see API 579-1/ASME FFS-1),

h) application of proper examination techniques, and

i) conducting pressure equipment integrity incident investigations (see API 585).

The information for each damage mechanism is provided in a set format as shown below.

— **Name of the Mechanism**—The term commonly used to describe or name the mechanism.

— **Description of Damage**—A basic description of the damage mechanism.

— **Affected Materials**—A list of the materials prone to the damage mechanism.

— **Critical Factors**—A list of factors that affect the damage mechanism (i.e. rate of damage).

— **Affected Units or Equipment**—A list of the affected equipment and/or units where the damage mechanism commonly occurs. This information is also shown on generic process flow diagrams (PFDs) for typical process units.

— **Appearance or Morphology of Damage**—A description of the damage mechanism, with pictures in some cases, to assist with recognition of the damage.

— **Prevention/Mitigation**—Methods to prevent or mitigate the damage and in some cases to evaluate by engineering analysis.

— **Inspection and Monitoring**—Guidance for nondestructive examination (NDE) and other methods for detecting, monitoring, characterizing, sizing, and determining the severity or extent of damage or deterioration.

— **Related Mechanisms**—A list of related damage mechanisms.

— **References—**A list of references cited, relied upon, or that provide background and other pertinent information.

Generic PFDs are provided in Section 4 to assist the user in determining primary locations where some of the significant damage mechanisms are commonly found.

2 Terms and Definitions

2.1 Definitions

For the purposes of this document, the following definitions apply.

2.1.1
austenitic
A term that refers to a type of metallurgical structure (austenite) normally found in 300 series stainless steel (SS) and nickel-based alloys. These materials have a face centered cubic crystallographic structure and are generally nonmagnetic.

2.1.2
austenitic stainless steels
The 300 series SS, which commonly include Types 304, 304L, 304H, 309, 310, 316, 316L, 316H, 317, 317L, 321, 321H, 347, and 347H. The “L” and “H” suffixes refer to controlled ranges of low and high carbon content, respectively. These alloys are characterized by an austenitic structure.

2.1.3
carbon steel
An alloy consisting primarily of iron (Fe) with a small amount of carbon (C). Carbon steels do not have alloying elements intentionally added. However, there may be small amounts of elements permitted by specifications such as ASTM A516 and ASTM A106, for example, that can affect corrosion-related properties, hardness after welding, and toughness. Elements that may be found in small quantities include Mn, Cr, Ni, Mo, Cu, S, Si, P, Al, V, and B.

2.1.4
diethanolamine
DEA
Chemical used in amine treating to remove H_2S and CO_2 from hydrocarbon streams.

2.1.5
diglycolamine
DGA
Chemical used in amine treating to remove H_2S and CO_2 from hydrocarbon streams.

2.1.6
duplex stainless steel
A family of stainless steels that contain a mixed austenitic-ferritic structure including Alloys 2205, 2304, and 2507. The welds of 300 series SS may also exhibit a duplex structure.

2.1.7
ferritic
A term that refers to a type of metallurgical structure (ferrite) normally found in carbon and low-alloy steels and many 400 series SS. These materials have a body centered cubic crystallographic structure and are generally magnetic.

2.1.8
ferritic stainless steels
A family of stainless steels including Types 405, 409, 410S, 430, 442, and 446.

2.1.9
heat-affected zone
HAZ
The portion of the base metal adjacent to a weld that has not been melted, but in which the metallurgical microstructure and mechanical properties have been changed by the heat of welding, sometimes with undesirable effects.

2.1.10
high-strength low-alloy steel
HSLA steel
A family of carbon steels in which higher strength levels are achieved by the addition of moderate amounts of alloying elements such as titanium, vanadium, or niobium in amounts of less than 0.1 %. They can be more sensitive to cracking during fabrication from hydrogen embrittlement (HE) (delayed cracking; also known as underbead cracking).

2.1.11
low-alloy steel
A family of steels containing up to 9 % chromium and other alloying additions for high temperature strength and creep resistance. The low-alloy steels commonly encountered in refining include C-0.5Mo, Mn-0.5Mo, 1Cr-0.5Mo, 1.25Cr-0.5Mo, 2.25Cr-1.0Mo, 5Cr-0.5Mo, and 9Cr-1Mo. These are considered ferritic steels, although their microstructures might be an alteration of the ferrite phase found in carbon steel.

2.1.12
martensitic
A term that refers to a type of hard metallurgical structure (martensite) normally found in some 400 series SS. Heat treatment or welding followed by rapid cooling can sometimes produce this or a similar hard metallurgical structure in carbon and low-alloy steels. Martensitic and similar hard microstructures typically need to be tempered by heat treatment to soften them in order to make the material suitable for use in refining applications.

2.1.13
martensitic stainless steel
A family of stainless steels including Types 410, 416, 420, 440A, 440B, and 440C.

2.1.14
methyl diethanolamine
MDEA
Chemical used in amine treating to remove H_2S and CO_2 from hydrocarbon streams.

2.1.15
monoethanolamine
MEA
Chemical used in amine treating to remove H_2S and CO_2 from hydrocarbon streams.

2.1.16
nickel-based
A family of alloys containing nickel as a major alloying element (>30 % Ni) including Alloys 200, 400, K-500, 800, 800H, 825, 600, 600H, 617, 625, 718, X-750, and C276.

2.1.17
stainless steel
An alloy of iron (Fe) with at least 10.5 % chromium (Cr) plus other alloy additions, depending on the specific grade. There are four major categories of stainless steels that are characterized by their metallurgical structure at room temperature: austenitic, ferritic, martensitic, and duplex. These alloys have varying amounts of chromium and other alloying elements that give them resistance to certain types of degradation depending on the alloy.

2.2 Acronyms and Abbreviations

For the purposes of this document, the following acronyms and abbreviations apply.

ABSA	angle beam spectral analysis
ACFM	alternating current field measurement
ACSCC	alkaline carbonate stress corrosion cracking
AET	acoustic emission testing
AGO	atmospheric gas oil
Al	aluminum
ARH	acid relief header
ARN	acid relief neutralizer
ASCC	alkaline stress corrosion cracking
AUBT	automated ultrasonic backscatter testing
AUT	automated ultrasonic testing
B	boron
BFW	boiler feedwater
C	carbon
C3	chemical symbol referring to propane or propylene
C4	chemical symbol referring to butane or butylene
Cat	catalyst or catalytic
CCR	continuous catalytic reforming
CH_4	methane
Cl^- SCC	chloride stress corrosion cracking
CO	carbon monoxide
CO_2	carbon dioxide

Cr	chromium
Cu	copper
CuF	cuprous fluoride
CuF_2	cupric fluoride
CUI	corrosion under insulation
CVN	Charpy V-notch
CW	cooling water
DEA	diethanolamine
DGA	diglycolamine
DIPA	diisopropylamine
DMW	dissimilar metal weld
DNB	departure from nucleate boiling
ECT	eddy current testing
EMAT	electromagnetic acoustic transducer
FAC	flow accelerated corrosion (in boiler water and steam condensate)
FCC	fluid catalytic cracker
Fe	iron
Fe_3O_4	magnetite
FeS	iron sulfide
FFS	Fitness-For-Service
FGE	fuel grade ethanol
FMR	field metallographic replication
FRP	fiber-reinforced plastic
GWT	guided wave testing
H_2	diatomic hydrogen gas
HAZ	heat-affected zone
HB	Brinell hardness number
HCGO	heavy coker gas oil
HCl	hydrochloric (acid)
HCN	hydrogen cyanide
H_2CO_3	carbonic acid

HE	hydrogen embrittlement
HF	hydrofluoric (acid)
Hg	mercury
HHPS	hot high-pressure separator
HIC	hydrogen-induced cracking
HP	high pressure
HPS	high-pressure separator
HRC	Rockwell hardness number (based on Rockwell C scale)
HRSG	heat-recovery steam generator
H_2S	hydrogen sulfide
HSAS	heat stable amine salts
HSLA	high-strength low-alloy
H_2SO_4	sulfuric acid
HCO	heavy cycle oil
HTHA	high-temperature hydrogen attack
HVGO	heavy vacuum gas oil
ID	inside diameter
IOW	integrity operating window
IRIS	internal rotating inspection system
K.O. or KO	knock out, as in K.O. drum
KOH	potassium hydroxide
LCGO	light coker gas oil
LCO	light cycle oil
LP	low pressure
LPS	low-pressure separator
LVGO	light vacuum gas oil
MAWP	maximum allowable working pressure
MDEA	methyl diethanolamine
MDMT	minimum design metal temperature
MEA	monoethanolamine
MFL	magnetic flux leakage

MIC	microbiologically influenced corrosion
Mn	manganese
Mo	molybdenum
MPT	minimum pressurization temperature
mpy	mils per year
MT	magnetic particle testing
MVP	materials verification program
Na	sodium
NAC	naphthenic acid corrosion
NaOH	sodium hydroxide
Nb	niobium
NDE	nondestructive examination
NFT	near-field testing
NH_3	ammonia
NH_4HS	ammonium bisulfide
Ni	nickel
NO_2	nitrogen dioxide
NPSH	net positive suction head
O_2	oxygen
OD	outside diameter
P	phosphorus
PAUT	phased array ultrasonic testing
PEC	pulsed eddy current
PFD	process flow diagram
PMI	positive materials identification
POX	partial oxidation
PREN	pitting resistance equivalent number
PT	liquid penetrant testing
PTA SCC	polythionic acid stress corrosion cracking
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride

PWHT	postweld heat treatment
RE	residual element
RFT	remote field testing
RT	radiographic testing
S	sulfur
SAW	submerged-arc welding
SCC	stress corrosion cracking
SEM	scanning electron microscope
Si	silicon
SLOFEC	saturated low-frequency eddy current
SO_2	sulfur dioxide
SOHIC	stress-oriented hydrogen-induced cracking
SRB	sulfate-reducing bacteria
SRC	stress relaxation cracking
SRU	sulfur recovery unit
SS	stainless steel
SSC	sulfide stress cracking
SW	sour water
SWS	sour water stripper
SWUT	shear wave ultrasonic testing
TAN	total acid number
Ti	titanium
TOFD	time of flight diffraction
UT	ultrasonic testing
UTS	ultimate tensile strength
V	vanadium
VT	visual inspection (visual testing)
WFMT	wet fluorescent magnetic particle testing
Zn	zinc

3 Damage Mechanisms

This section describes the damage mechanisms found in refinery equipment. It includes low- and elevated-temperature corrosion, metallurgical and mechanical damage, environment-assisted cracking, and a few mechanisms that do not necessarily fit into any of these categories.

Section 4 contains PFDs for process units commonly found in refining. These PFDs show the location in the unit where specific damage mechanisms are most likely to be found.

3.1 885 °F (475 °C) Embrittlement

3.1.1 Description of Damage

885 °F (475 °C) embrittlement is a loss of ductility and fracture toughness due to a metallurgical change that can occur in stainless steels containing a ferrite phase as the result of exposure in the temperature range 600 °F to 1000 °F (315 °C to 540 °C). The embrittlement can lead to cracking failure.

3.1.2 Affected Materials

a) 400 series SS (e.g. 405, 409, 410, 410S, 430, and 446).

b) Duplex stainless steels such as Alloys 2205, 2304, and 2507.

c) Austenitic (300 series) stainless steel weld metals, which normally contain up to about 10 % ferrite phase to prevent hot cracking during welding.

3.1.3 Critical Factors

a) The alloy composition, particularly chromium content, amount of ferrite phase, and operating temperature are critical factors.

b) The lower-chromium alloys (e.g. 405, 409, 410, and 410S) are less susceptible to embrittlement. The higher chromium ferritic stainless steels [e.g. 430 (16 % to 18 % Cr) and 446 (23 % to 27 % Cr)] and duplex stainless steels (22 % to 25 % Cr) are much more susceptible.

    1. Although it has not yet been shown in all 300 series SS weld metals, Charpy impact testing of Type 308 and Type 347H SS weld metal aged in approximately the 850 °F to 885 °F (455 °C to 475 °C) temperature range has found evidence of 885 °F (475 °C) embrittlement, with individual sample results in some cases being less than 15 ft-lb (20 J) at ambient temperatures. However, 885 °F (475 °C) embrittlement of austenitic stainless steel weld metal historically has not been found to be a significant concern in typical refining applications.

c) Increasing amounts of ferrite phase in duplex stainless steels increase susceptibility to damage when operating in the high-temperature range of concern. A dramatic increase in the ductile-to-brittle transition temperature will occur. Duplex stainless steels also need to be cooled rapidly after welding to avoid formation of embrittling phases.

d) High-temperature exposure is required for embrittlement. A primary consideration is operating time at temperature within the critical temperature range. Damage is cumulative and results from the formation of an embrittling ordered metallic phase (alpha prime phase) that occurs most readily at approximately 885 °F (475 °C). Additional time is required to reach maximum embrittlement at temperatures above or below 885 °F (475 °C). For example, many thousands of hours may be required to cause embrittlement at 600 °F (315 °C).

e) As a practical matter, since equipment is typically in service for years, it is often assumed that susceptible materials that have been exposed to temperatures in the 600 °F to 1000 °F (370 °C to 540 °C) range are affected.

f) The effect on toughness is not pronounced at the operating temperature but is significant at lower temperatures experienced during plant shutdowns, start-ups, or upsets.

g) Embrittlement can also result from heat treatment if the material is held within or cooled slowly through the embrittlement range.

3.1.4 Affected Units or Equipment

a) 885 °F (475 °C) embrittlement can be found in any unit where susceptible alloys are exposed to the embrittling temperature range.

b) Most refining companies limit the use of ferritic stainless steels to non-pressure-boundary applications because of this damage mechanism.

c) Common examples include fractionator trays and internals in high-temperature vessels used in crude, vacuum, fluid catalytic cracker (FCC), and coker units. Typical failures include cracking when attempting to weld or to straighten bent, upset tower trays made of Type 409 and 410 SS. (This occurs often with vacuum tower trays of this material.)

d) Other examples include duplex stainless steel heat exchanger tubes and other components exposed to temperatures above 600 °F (315 °C) for extended time periods. Duplex stainless steels are normally limited to a maximum service temperature of 600 °F (315 °C).

3.1.5 Appearance or Morphology of Damage

a) 885 °F (475 °C) embrittlement is a metallurgical change that is not readily apparent with metallography.

b) The existence of 885 °F (475 °C) embrittlement can possibly be identified by an increase in hardness in affected areas. Failure during bend testing or impact testing of samples removed from service is the most positive indicator of 885 °F (475 °C) embrittlement. (Figure 3-1-1)

c) Most cases of embrittlement are found in the form of cracking during turnarounds or during start-up or shutdown when the material is at lower temperature where the effects of embrittlement are most detrimental. Embrittled 410 SS has been shown to require a temperature of about 350 °F (175 °C) before adequate toughness has been restored.

3.1.6 Prevention/Mitigation

a) The best way to prevent 885 °F (475 °C) embrittlement is to avoid exposing the susceptible material to the embrittling range or to use a non-susceptible material. In some cases, users accept the possibility of embrittlement of non-pressure-containing components, e.g. trays and other internals, and deal with the possibility or consequences during maintenance.

b) Cracking of embrittled material can often be avoided through temperature controls during start-up and shutdown.

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

d) 885 °F (475 °C) embrittlement is reversible by heat treatment followed by rapid cooling. The de-embrittling heat treatment temperature is typically 1100 °F (595 °C) or higher and may not be practical for many equipment items. If the de-embrittled component is exposed to the same service conditions, it will re-embrittle faster than it did initially.

3.1.7 Inspection and Monitoring

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

a) The most effective method of detecting or confirming 885 °F (475 °C) embrittlement is removing and impact or bend testing a sample of the suspect material. Failure during a simple bend test is the most common

method of confirming 885 °F (475 °C) embrittlement in thin components like tower trays. Metallographic examination is typically not effective because the embrittlement-causing phase in the microstructure is so difficult to find or see.

b) Cracking may be visually apparent in certain types of trays and other non-pressure-containing hardware that have cracked during maintenance or repair activities.

c) Field hardness testing may distinguish embrittled from non-embrittled material, but hardness testing alone is generally not definitive. Also, the hardness test itself may produce cracking, depending on the degree of embrittlement.

d) Hammer testing ("field impact testing") is considered a destructive test. Tapping a suspect component with a hammer may crack the component, depending on the degree of embrittlement. Hammer testing might confirm that a component is not badly embrittled, if it does not crack, or that it is embrittled, if it does crack.

3.1.8 Related Mechanisms

Sigma phase embrittlement (3.56).

3.1.9 References

1. *High-temperature Characteristics of Stainless Steels*, *Designers' Handbook Series*, American Iron and Steel Institute, Washington, DC, 1979.

2. G.E. Moller, "Experiences with 885 °F (475 °C) Embrittlement in Ferritic Stainless Steels," *Materials Protection*, NACE International, May 1966.

3. S.A. David, J.M. Vitek, and D.J. Alexander, "Embrittlement of Austenitic Stainless Steel Welds," Office of Scientific and Technical Information Technical Reports, (University of North Texas Libraries Government Documents Department, https://digital.library.unt.edu/ark:/67531/metadc741815/), June 1995.

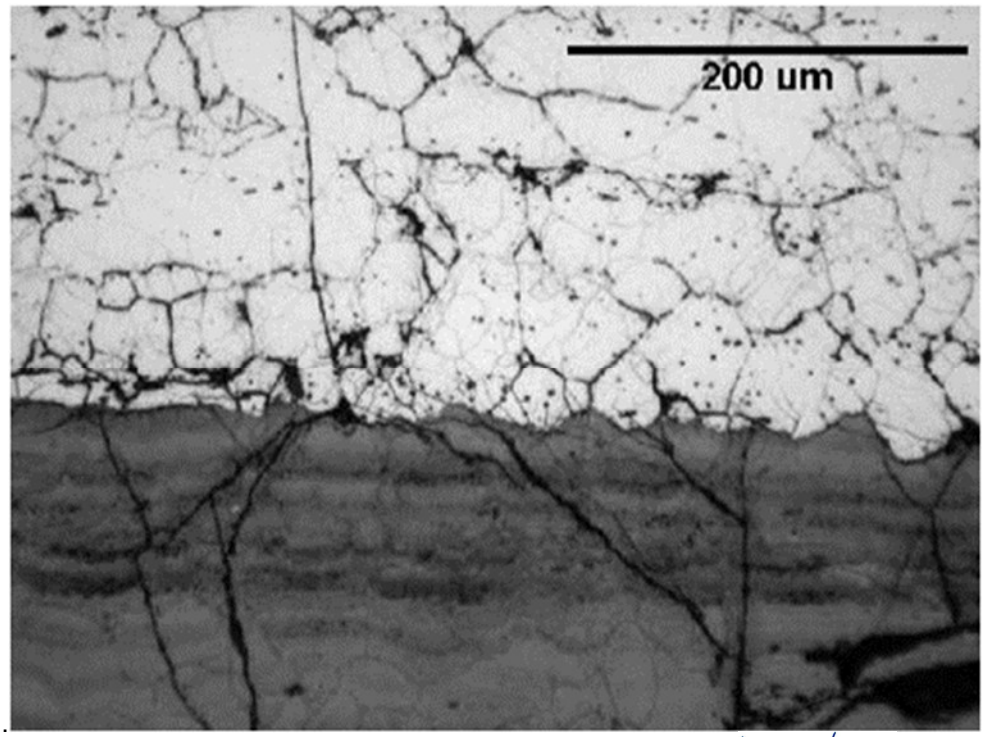


Figure 3-1-1—Sample of cracked material with intergranular cracks visible in the microstructure, suggesting severe embrittlement.

3.2 Amine Corrosion

3.2.1 Description of Damage

a) Amine corrosion is typically localized corrosion that occurs principally on carbon steel in amine treating processes. Corrosion is not caused by the amine itself but results from dissolved acid gases (CO_2 and H_2S), heat stable amine salts (HSAS), amine degradation products (e.g. bicine, oxalate, and formate salts), and other contaminants.

b) SCC of carbon steel in amine services is discussed in 3.3.

3.2.2 Affected Materials

Primarily carbon steel. 300 series SS and other grades of stainless steel are more resistant.

3.2.3 Critical Factors

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

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

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

d) Lean amine solutions are generally not corrosive because they have low conductivity and high pH. However, an excessive accumulation of heat stable salts, e.g. bicine, oxalate, formate, and acetate salts above about 2 %, depending on the amine, can significantly increase corrosion rates in hot lean amine.

e) Oxygen in-leakage causes high corrosion rates and contributes to heat stable salt formation.

f) Lean amine solutions contain a small amount of H_2S, which helps maintain a stable iron sulfide film. Overstripped lean amine solutions can be corrosive if there is inadequate H_2S present to maintain the protective iron sulfide film.

g) Corrosion rates increase with increasing temperature, particularly in rich amine service. Temperatures above about 220 °F (105 °C) can result in acid gas flashing, if the pressure drop is high enough, with severe localized corrosion.

h) Process stream velocity will influence the amine corrosion rate and nature of attack. Corrosion is generally uniform; however, high velocities and turbulence will cause localized thickness losses. For carbon steel, velocities are generally limited to 3 fps to 6 fps (1 m/s to 2 m/s) for rich amine and about 20 fps (6 m/s) for lean amine.

3.2.4 Affected Units or Equipment

a) Amine units, which remove H_2S, CO_2, and mercaptans from process streams in many units including crude, coker, FCC, hydrogen-reforming, hydroprocessing, and tail gas units.

b) The regenerator reboiler, including the feed and return lines, and the regenerator are areas where the temperature and turbulence are the highest in the amine system and therefore are locations of potentially significant corrosion.

1. If excessive regeneration occurs in the reboiler (i.e. > 5 % of the total amine regeneration occurs in the reboiler), it can lead to acid gas corrosion in the reboiler, its vapor return line, and the bottom of the regenerator.

2. Ammonia, H_2S, and hydrogen cyanide (HCN) accelerate corrosion in the regenerator overhead condenser and outlet piping as well as reflux piping, valves, and pumps.

c) The rich amine side of the lean/rich exchangers, the hot lean amine piping, the hot rich amine piping, the stripper overhead condenser piping, the amine solution pumps, and the reclaimers are also areas where corrosion problems commonly occur.

d) In amine absorber systems, the locations most susceptible to amine corrosion are where amine or acid gas impinge on the shell, as well as downstream of pressure letdown valves and other areas of high velocity in the rich amine piping.

3.2.5 Appearance or Morphology of Damage

a) Carbon steel and low-alloy steels mostly suffer uniform thinning in localized (isolated) locations or localized under-deposit attack. (Figure 3-2-1 to Figure 3-2-6)

b) When the process stream velocity is low, thinning will be more uniform and widespread. At locations with high velocity or turbulence, it will be more localized with greater metal loss.

c) Welds can be preferentially attacked. (Figure 3-2-1 and Figure 3-2-3)

3.2.6 Prevention/Mitigation

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

b) Proper attention should be given to avoiding the buildup of heat stable salts to unacceptable levels.

c) The system design should incorporate measures to control local pressure drop to minimize flashing. In areas where it is unavoidable, upgrading to 300 series SS or other corrosion-resistant alloys may be needed. Type 410 SS trays and internals are commonly used in absorber and stripping towers.

d) Avoid air ingress into the system as this will lead to formation of corrosive heat stable salts.

e) Storage tanks and surge vessels should be blanketed with oxygen-free inert gas to prevent introduction of oxygen and in-leakage of air.

f) Solids and hydrocarbons should be removed from the amine solution by filtration and through process control.

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

3.2.7 Inspection and Monitoring

a) Visual inspection (VT) of internal surfaces at flow impingement areas, turbulent flow areas, liquid/vapor interfaces, and of welds/heat-affected zones (HAZs) is effective in identifying localized corrosion. Sometimes a pit gauge is used in conjunction with visual examination to provide specific data on extent of metal loss.

b) Thin regions:

1. external ultrasonic testing (UT) is typically used to map the thickness of components to identify local thin regions;

2. profile radiographic testing (RT) can be effective for identifying localized attack, particularly at welds/HAZs and turbulent locations;

3. UT can sometimes be used in conjunction with VT, laser scanning, structured white light imaging, and/or pit gauges to determine the extent of metal loss.

c) Permanently mounted thickness monitoring sensors can be used.

d) Corrosion monitoring can be performed by installing corrosion coupons and/or inserting corrosion probes.

e) The level of amine degradation products (e.g. bicine, oxalate, and formate salts), should be monitored. An increase in iron content of the amine solution will coincide with an increase in the level of these degradation products.

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

3.2.8 Related Mechanisms

Amine SCC (3.3).

3.2.9 References

1. J. Gutzeit, “Refinery Corrosion Overview,” *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, 1986, pp. 171–189.

2. L.R. White and D.E. Street, “Corrosion Control in Amine Treating Units,” *Proceedings of the Special Symposium on Corrosion in the Oil Refining Industry*, NACE International, Houston, TX, 1996.

3. R.B. Nielsen et al., “Corrosion in Refinery Amine Systems,” Paper No. 571, *Corrosion/95*, NACE International, Houston, TX.

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

5. M.A. Saleem and A.A. Hulaibi, “Corrosion Challenges in Gas Treating Units,” Paper No. 08416, *Corrosion/2008*, NACE International, Houston, TX.

6. P. Quiroga et al., “Improving Amine Unit Reliability with On-line Corrosion Monitoring & Modeling,” Paper No. 08421, *Corrosion/2008*, NACE International, Houston, TX.

7. D. Fan et al., “Role of Impurities and H_2S in Refinery Lean DEA System Corrosion,” Paper No. 00495, *Corrosion/2004*, NACE International, Houston, TX.

Figure 3-2-1—Localized amine corrosion at the weld found in piping from the reboiler to the regenerator tower in an MEA unit. Many other similar cases were found, some going as deep as half thickness. They were originally found with shear wave UT inspection and mistaken as cracks.

Figure 3-2-2—Hot lean amine corrosion of carbon steel attributed to increased CO_2 content in the MEA solution.

Figure 3-2-3—Preferential weld corrosion in lean amine. (Reference 5)

Figure 3-2-4—Preferential corrosion in an amine regenerator reboiler return elbow. (Reference 6)

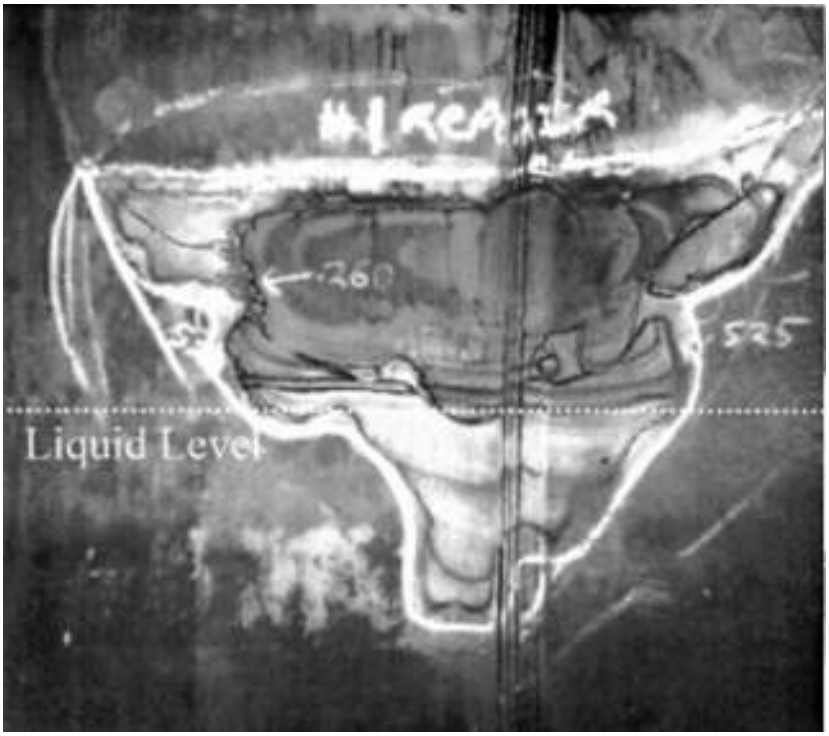


Figure 3-2-5—Corrosion near the liquid level in a reboiler exchanger shell from an amine regeneration unit. (Numbers drawn on figure are UT thicknesses in inches.) Nominal wall: 0.550 in. (Reference 7)

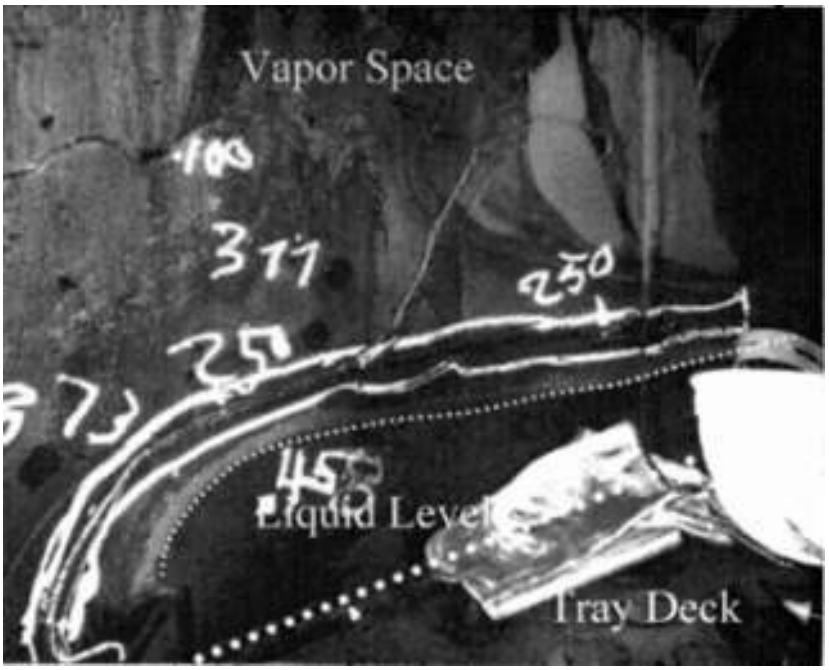


Figure 3-2-6—Corroded amine regenerator column shell near a downcomer. (Numbers drawn on figure are UT thicknesses in inches.) Nominal wall: 0.5 in. (Reference 7)

3.3 Amine Stress Corrosion Cracking

3.3.1 Description of Damage

a) Amine SCC (or amine cracking) is the cracking of steels under the combined action of tensile stress and an aqueous alkanolamine solution used to remove (absorb) H_2S and/or CO_2 and their mixtures from various gas and liquid hydrocarbon streams.

b) Amine cracking is a form of alkaline stress corrosion cracking (ASCC).

c) It is most often found at or adjacent to non-postweld-heat-treated (non-PWHT'd) carbon steel welds or in highly cold worked parts.

d) Amine cracking should not be confused with several other types of SCC that can occur in amine environments, which are further described in 3.66 and 3.12.

3.3.2 Affected Materials

Carbon steel and low-alloy steels.

3.3.3 Critical Factors

a) The critical factors are the level of tensile stress, the type of amine, and temperature.

b) Increasing stress level increases the likelihood and severity of cracking. Cracking is most often associated with high residual stresses from welding or cold working that have not been removed by an effective stress-relieving heat treatment.

c) Cracking is more likely to occur in MEA and DEA services, but is also found in most amines including MDEA and DIPA (ADIP).

d) Increasing temperature increases the likelihood and severity of cracking; however, cracking has been reported down to ambient temperatures with some amines, MEA in particular. Other than in special cases (such as where the steel component is completely clad or overlayed with stainless steel or other alloy and the welds are not exposed), PWHT is now commonly recommended for all lean amine systems (excluding fresh amine) at all operating temperatures, regardless of amine type. Some refiners also PWHT'd rich amine service equipment, whether for amine SCC resistance, wet H_2S [SSC and stress-oriented hydrogen-induced cracking (SOHIC)] resistance, or both. Refer to API 945 for guidelines on PWHT for various amine services.

e) Amine cracking is most often associated with lean amine services, where a solution of amine and water is used. The pure alkanolamine does not cause cracking. In rich amine services in H_2S removal systems, the H_2S helps form an iron sulfide (FeS) film on steel surfaces that helps impede amine SCC. Cracking in rich amine services is most often associated with wet H_2S. (See 3.67.)

f) Cracking can occur in non-PWHT'd piping and equipment as the result of exposure to steam out and to short-term amine carryover. This is another reason PWHT (for stress relief) is now commonly recommended regardless of operating temperature.

g) Amine concentration does not appear to have a significant effect on the propensity for cracking.

3.3.4 Affected Units or Equipment

All non-PWHT'd carbon steel piping and equipment in amine service, including contactors, absorbers, strippers, filters, regenerators, and heat exchangers, as well as any equipment subject to amine carryover, are subject to cracking. Equipment in rich amine service is less susceptible than equipment in lean amine service, but not necessarily immune, especially vessels where acid gas is either entering the amine (making rich amine) or leaving the amine (making lean amine).

3.3.5 Appearance or Morphology of Damage

a) Amine SCC cracks initiate on the (process side) surface of piping and equipment, primarily at welds. Cracks can appear in the HAZ and/or the weld metal but are most often found in the high residual stress zone, which is typically beyond the metallurgical HAZ, about a tenth of an inch or more (several millimeters) from the weld. (Figure 3-3-1)

b) Cracking typically develops parallel to the weld, and there may be multiple parallel cracks. In weld metal, the cracks are either longitudinal or transverse to the weld.

c) At set-on nozzles, the cracks are radial in the base metal, i.e. they fan out from the bore. (Figure 3-3-2)

d) At set-in nozzles, the cracks are usually parallel to the weld.

e) The appearance of the cracks on the surface may be similar to those caused by wet H_2S cracking.

f) Because residual stress is a driving force for cracking, cracks can occur on the process side opposite external attachment welds.

g) Positive identification of amine cracking can be confirmed by metallographic analysis. The cracking is typically intergranular and oxide filled with some branching. (Figure 3-3-1 and Figures 3-3-3 to 3-3-5)

3.3.6 Prevention/Mitigation

a) Carbon steel welds in piping and equipment should be stress relieved in accordance with API 945 and NACE SP0472. The recommended minimum stress-relief temperature is 1175 ± 25 °F (635 ± 15 °C). The same recommendation applies to repair welds and to internal and external attachment welds. (See Figure 3-3-6.) For local PWHT, recommended heat treatment band width is listed in NACE SP0472 with reference to WRC 452.

b) Consider using solid or clad stainless steel or other corrosion-resistant alloys in lieu of carbon steel.

c) Thoroughly water wash non-PWHT'd carbon steel piping and equipment prior to welding, heat treatment, or steam out.

3.3.7 Inspection and Monitoring

a) Wet fluorescent magnetic particle testing (WFMT), alternating current field measurement (ACFM), and eddy current testing (ECT) can be effective techniques to detect these surface-breaking cracks. Proper surface preparation by grit blasting, high-pressure water blasting, flapper wheel abrasive grinding, or other method is required to remove scale and contaminants. The method of surface preparation is dependent upon the specific technique.

b) Angle beam [shear wave ultrasonic testing (SWUT) and phased array ultrasonic testing (PAUT)] ultrasonic techniques can be effective to detect and size cracks and would be the methods typically used for piping; however, caution must be exercised when interpreting results on piping welds that have not previously been inspected with angle beam UT (SWUT or PAUT) as it may be difficult to distinguish SCC from original fabrication flaws. SWUT and PAUT can also be used to periodically monitor crack growth.

c) Liquid penetrant testing (PT) may be used but should not be the only means of detection. PT may not be effective in finding tight cracks because the cracks are oxide filled.

d) RT may not be effective in detecting fine, tight cracks.

e) Acoustic emission testing (AET) can be used for locating cracks and monitoring crack growth.

3.3.8 Related Mechanisms

Caustic SCC (3.15) and carbonate SCC (3.12) are other forms of ASCC that are similar in appearance. Ammonia SCC of carbon steel (3.4) is also similar in appearance.

3.3.9 References

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

2. "Fitness-For-Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service," Materials Properties Council, FS-26, Draft No. 5, Consultants Report, NY, 1995.

3. J. Gutzeit and J.M. Johnson, "Stress Corrosion Cracking of Carbon Steel Welds in Amine Service," *Materials Performance*, Vol. 25, No. 7, 1986, p.18.

4. J.P. Richert et al., "Stress Corrosion Cracking of Carbon Steel in Amine Systems," Paper No. 187, *Corrosion/87*, NACE International, Houston, TX.

5. A. Bagdasarian et al., "Stress Corrosion Cracking of Carbon Steel in DEA and ADIP Solutions," *Materials Performance*, 1991, pp. 63–67.

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

7. WRC Bulletin 452*, Recommended Practices for Local Heating of Welds in Pressure Vessels*, Welding Research Council, Shaker Heights, OH, June 2000.

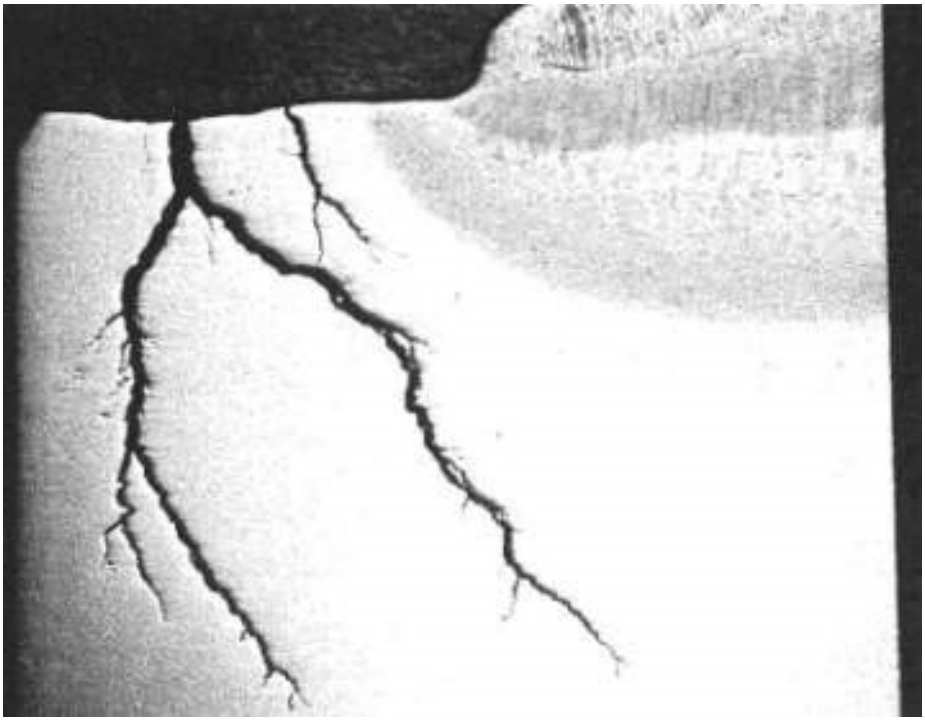


Figure 3-3-1—A photomicrograph of a cross section of a weld in non-PWHT'd carbon steel piping showing amine SCC in the vicinity of a piping weld. Magnification 6X (from API 945).

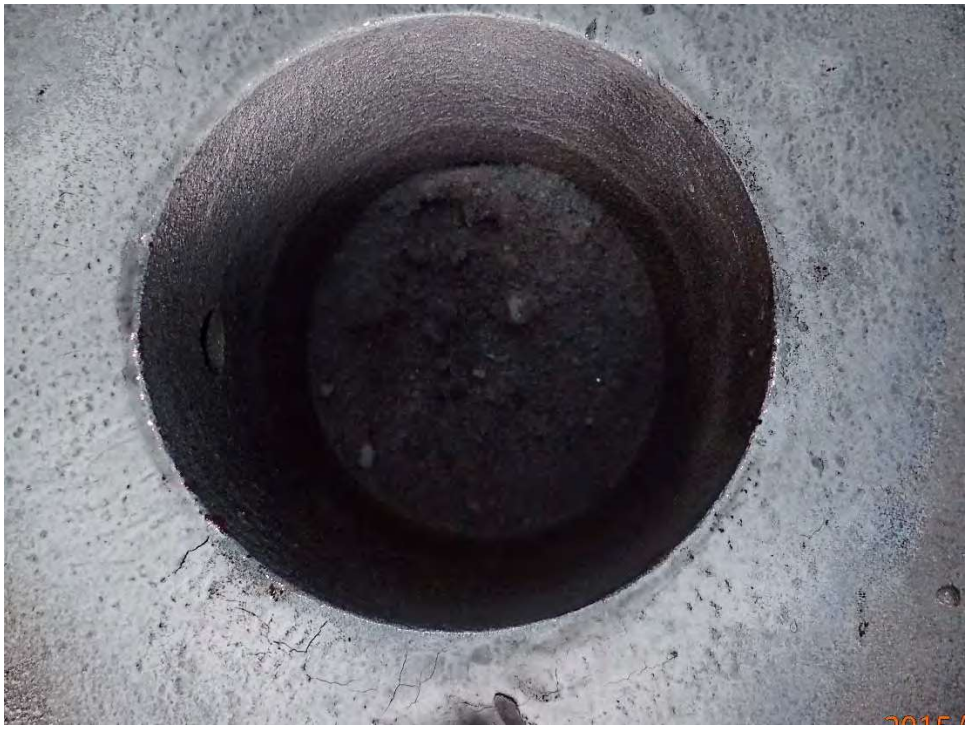


Figure 3-3-2—Radial amine SCC cracks emanating from the bore of a nozzle in a rich amine reboiler exchanger.

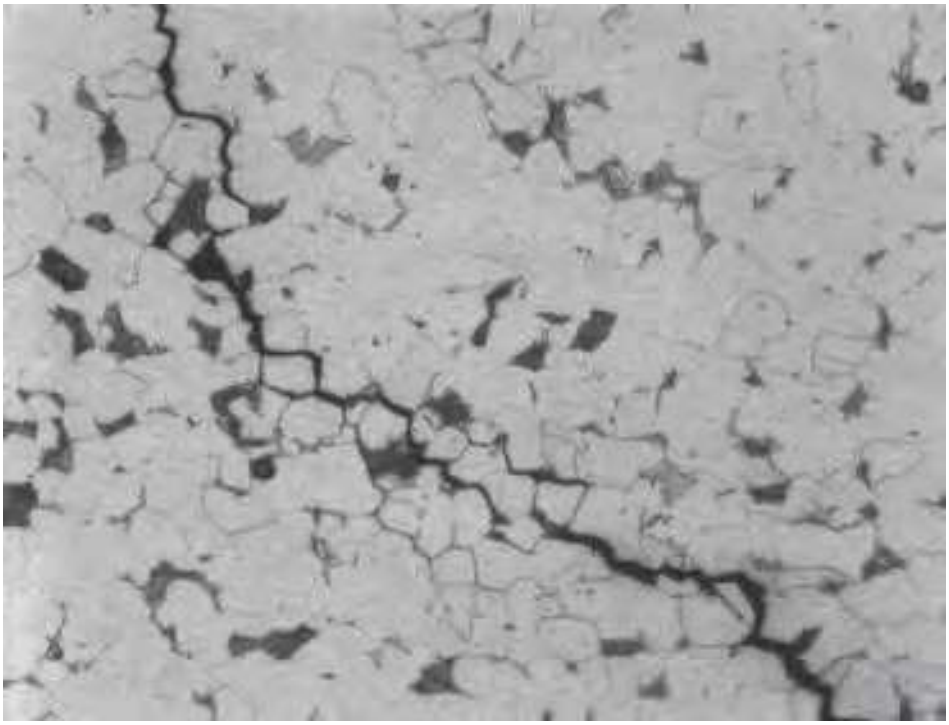


Figure 3-3-3—A higher-magnification view of the crack tip in Figure 3-3-1. Magnification 200X (from API 945).

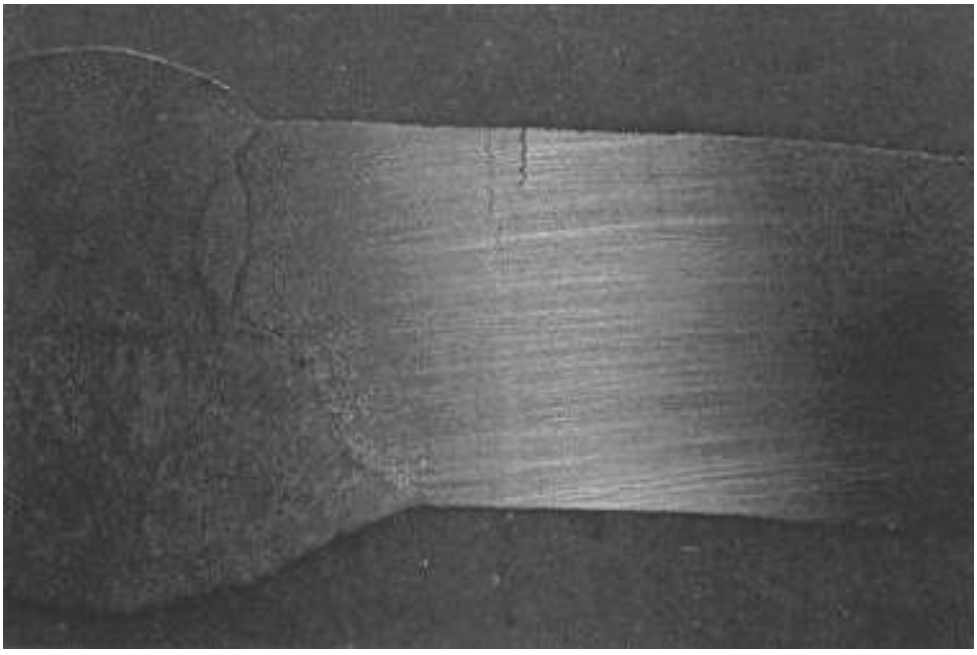


Figure 3-3-4—A photomicrograph of a cross section of a carbon steel piping weld showing amine SCC in a section of the line from the MEA absorber column normally operated at 100 °F (38 °C). Magnification 6X (from API 945).

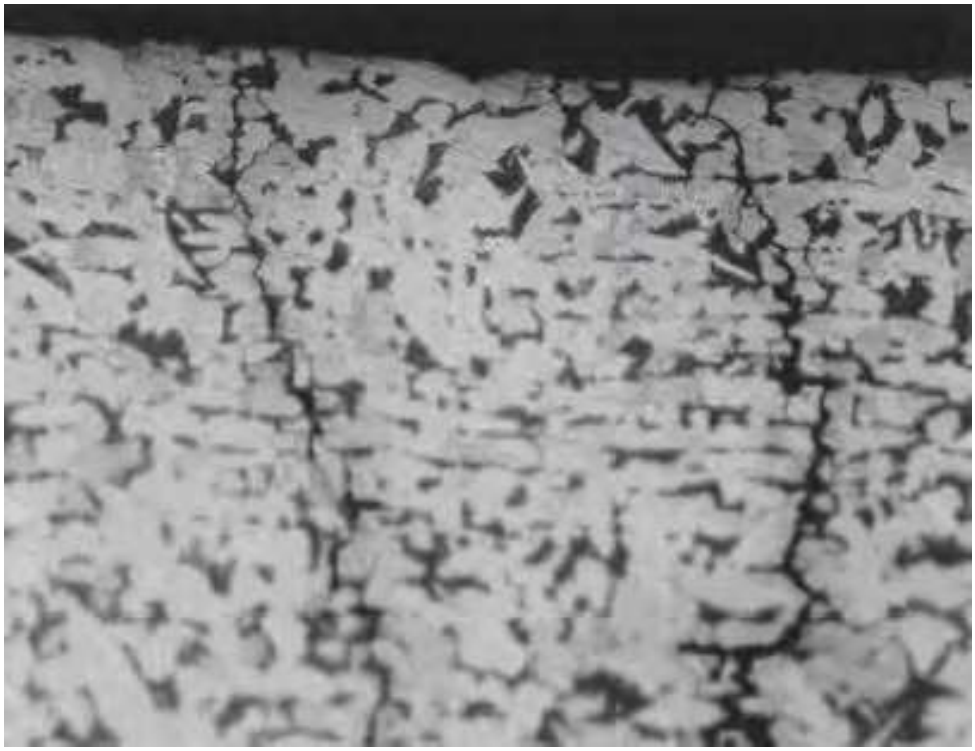


Figure 3-3-5—A higher-magnification view of the cracks in Figure 3-3-4, which illustrates the intergranular nature of the cracking. Magnification 200X (from API 945).

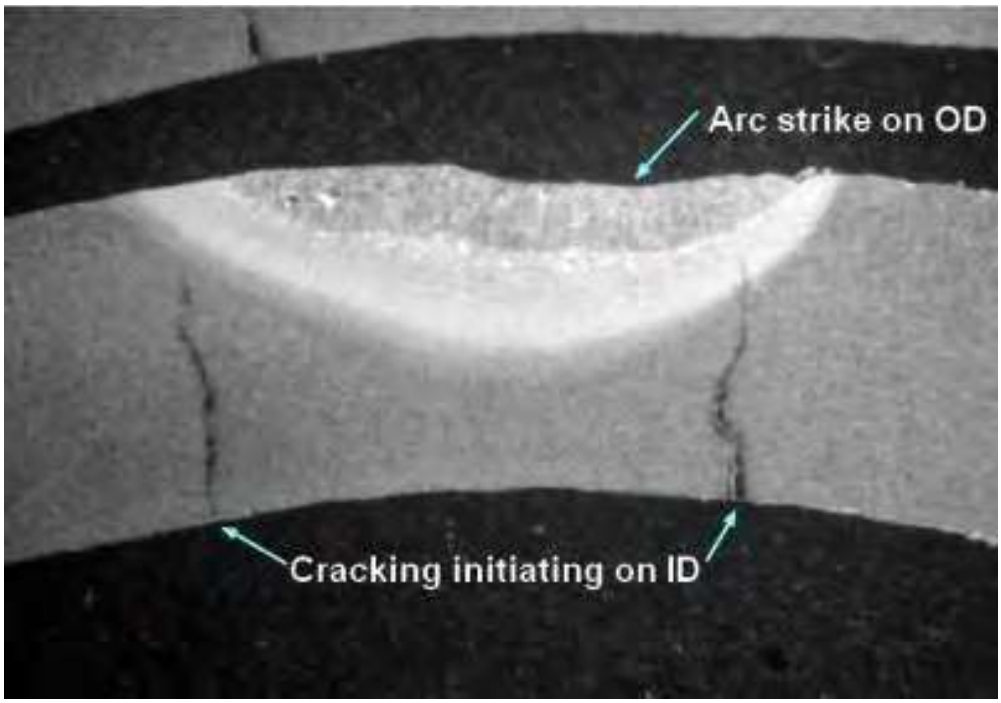


Figure 3-3-6—Amine SCC developed on the inside diameter (ID) beneath an arc strike on the outside diameter (OD) of a 3-in. line in 20 % MEA. The original line was PWHT'd during original fabrication but not the arc strike. Leaks occurred after 30 years of service.

3.4 Ammonia Stress Corrosion Cracking

3.4.1 Description of Damage

a) Aqueous streams containing ammonia may cause SCC in some copper alloys.

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

3.4.2 Affected Materials

a) Copper-zinc alloys (brasses, especially as zinc increases above 15 %), including admiralty brass and aluminum brasses, in environments with aqueous ammonia and/or ammonium compounds.

b) Carbon steel, especially high-strength steel, in anhydrous ammonia.

3.4.3 Critical Factors

a) For copper alloys:

1. susceptible alloys may suffer cracking under the combination of residual stress and exposure to ammoniated chemical compounds;
2. zinc content of brasses affects susceptibility, especially as zinc increases above 15 %;
3. a water phase with ammonia or ammoniacal compounds must be present;
4. oxygen is necessary, but trace amounts are sufficient;
5. pH needs to be above 8.5;
6. occurs at any temperature;
7. residual stresses from fabrication or tube rolling are sufficient to promote cracking.

b) For steel:

1. anhydrous ammonia with < 0.2 % water may cause cracking in carbon steel;
2. cracking has been reported as low as −27 °F (−33 °C) in laboratory testing; crack growth rates and cracking susceptibility increase with increasing temperature, but cracking can occur at ambient or refrigerated conditions;
3. stress relief after welding eliminates susceptibility of most common steels (those not greater than 70 ksi minimum specified tensile strength);
4. contamination with even small amounts of air or oxygen increases tendency toward cracking;
5. high residual stresses from fabrication and welding increase susceptibility.

3.4.4 Affected Units or Equipment

a) Copper-zinc alloy tubes in heat exchangers.

1. Ammonia is present as a process contaminant in some services or may be intentionally added as an acid neutralizer.
2. Ammonia can be present in cooling water.
3. Ammonia can be present in steam condensate and boiler feedwater (BFW) systems. Some chemicals used for treating BFW, including hydrazine, neutralizing amines, and ammonia-containing compounds, can lead to SCC if not properly controlled.

b) Non-stress-relieved carbon steel ammonia storage tanks, piping, and equipment in ammonia refrigeration units, as well as some lube oil refining processes.

3.4.5 Appearance or Morphology of Damage

a) Copper alloys.

1. Surface-breaking cracks may show bluish corrosion products.
2. Exchanger tubes show single or highly branched cracks on the surface.
3. Cracking can be either transgranular (Figure 3-4-1 and Figure 3-4-2) or intergranular (Figure 3-4-3), depending on the environment and stress level.

b) Carbon steel.

1. Cracking will occur at exposed non-stress-relieved welds and HAZs.
2. Cracking is primarily intergranular in nature.

3.4.6 Prevention/Mitigation

a) Copper alloys.

1. Copper-zinc alloys with < 15 % zinc have improved resistance.
2. The 90-10 Cu-Ni and 70-30 Cu-Ni alloys have very low susceptibility. Below 120 °F (50 °C), the cupro-nickels are immune for all practical purposes.
3. SCC in steam service can sometimes be controlled by preventing the ingress of air.
4. 300 series SS and nickel-based alloys are immune.

b) Carbon steel.

1. SCC of steel can be prevented through the addition of small quantities of water to the ammonia (0.2 % minimum). Be aware that vapor spaces could have less than 0.2 % water present due to partitioning of ammonia in water phase.
2. An effective stress relief of the welds reduces residual stress to the point where ammonia SCC can be prevented.
3. Low-strength steels (<70 ksi minimum specified tensile strength) should be used.
4. Prevent ingress of oxygen into storage facilities. Even low levels of oxygen (<5 ppm) have been reported to lead to cracking under some conditions. Oxygen levels should be maintained below 1 ppm.
5. Nitrogen can be used to purge oxygen prior to introduction of ammonia into atmospheric and pressurized storage systems.

3.4.7 Inspection and Monitoring

a) For copper alloys:

1. the pH and ammonia content of water draw samples should be monitored to assess susceptibility of copper alloys to determine extent of inspection;
2. heat exchanger tubes can be monitored for cracking using ECT or VT. PT can be applied in the rolled area, which is highly susceptible to cracking.

b) For carbon steel storage tanks (atmospheric or pressurized), vessels, and piping, in anhydrous ammonia:

1. WFMT is typically used on the welds and HAZs of storage tanks and pressure vessels and can also identify SCC in piping; alternatively, eddy current array testing can be used to perform these inspections;

2. angle beam UT (SWUT or PAUT) can be performed from the outside surface;

3. AET can be used for locating cracks and monitoring crack growth in vessels.

NOTE NH_3 SCC can occur parallel, transverse, or oblique to the weld and HAZ. NDE applied should be performed to detect various orientations of SCC.

3.4.8 Related Mechanisms

None.

3.4.9 References

1. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, p. 117.

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

3. A. Cohen, "Copper and Copper-base Alloys," *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, 1986, pp. 479–501.

4. NACE Publication 5A192, *Integrity of Equipment in Anhydrous Ammonia Storage and Handling*, NACE International, Houston, TX, 2004.

5. "Environmental Cracking," Materials Technology Institute, St. Louis, Missouri, 2016.

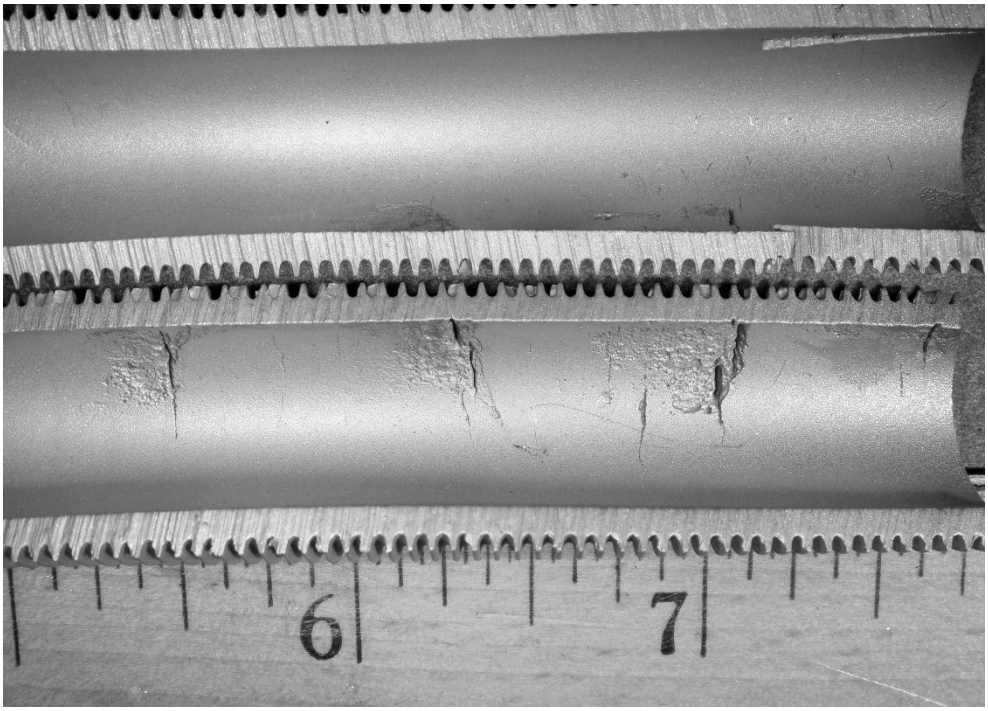


Figure 3-4-1—Ammonia SCC in an inhibited admiralty tube UNS C44300, 0.75 in. diameter, BWG 16 (0.063 in. thick) with extruded fins.

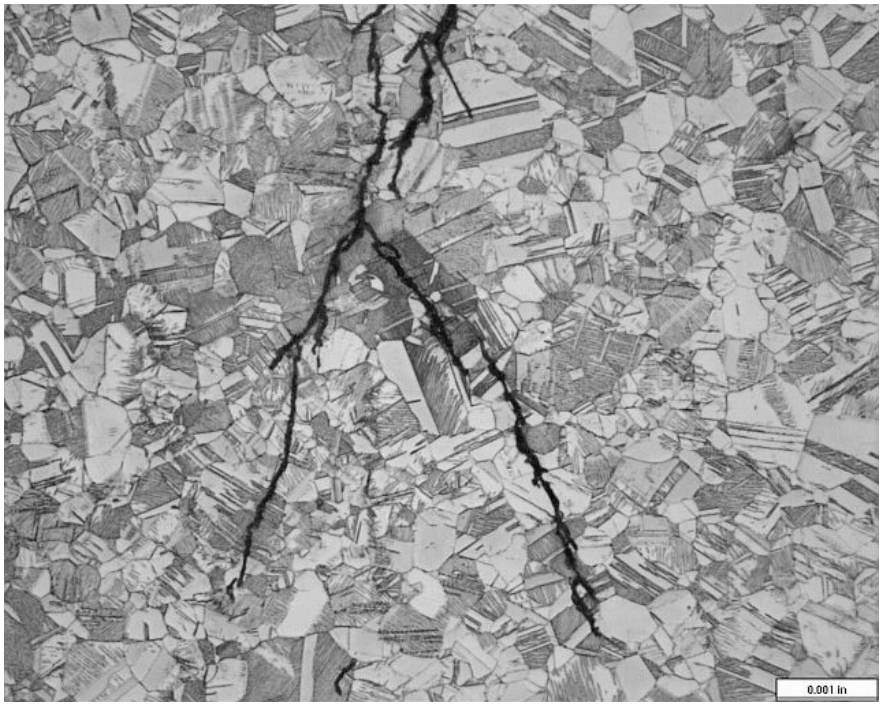


Figure 3-4-2—High-magnification view of a cross section of the tube in Figure 3-4-1 showing transgranular cracking. (Magnification 500X.)

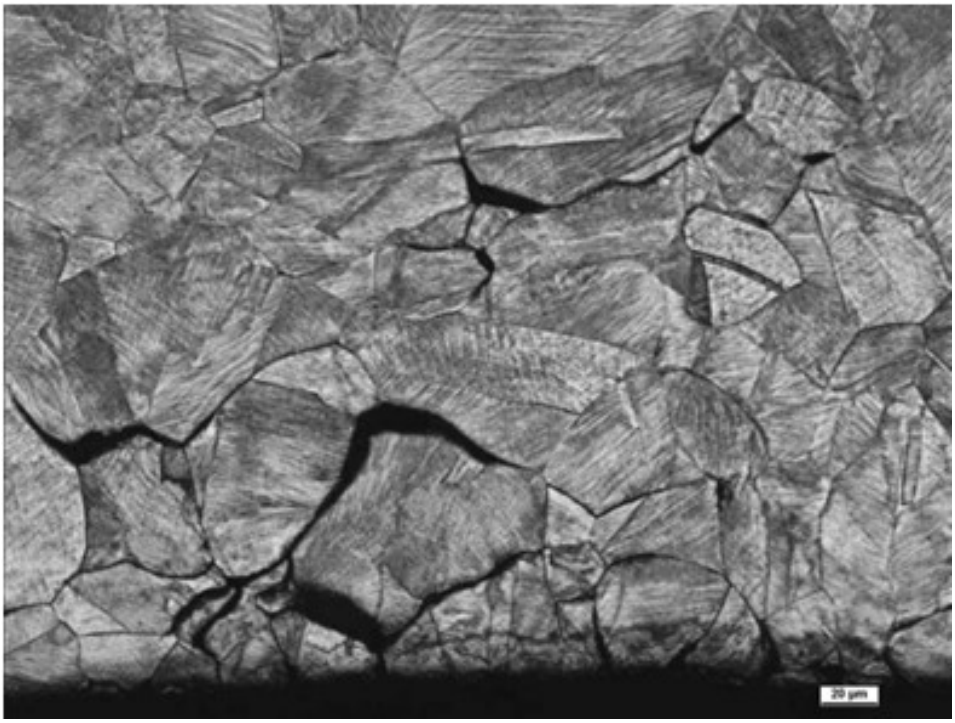


Figure 3-4-3—High-magnification view of a cross section of a brass exchanger tube showing intergranular cracking.

3.5 Ammonium Bisulfide Corrosion (Alkaline Sour Water)

3.5.1 Description of Damage

Aggressive corrosion occurring in hydroprocessing reactor effluent streams and in units handling alkaline sour water (SW), especially in areas of high turbulence.

3.5.2 Affected Materials

a) Carbon steel and low-alloy steels.

b) 300 series SS, duplex stainless steel, nickel-based alloys, and titanium and its alloys are more resistant, depending on ammonium bisulfide (NH_4HS) concentration and velocity.

1. Aluminum has been used for NH_4HS corrosion resistance in air coolers, but can suffer high corrosion rates in high-velocity or turbulent locations.

2. Titanium and its alloys have been used for NH_4HS corrosion resistance in air coolers but can suffer embrittlement from hydriding in these services. (See 3.66.)

3. Welds in duplex stainless steel can be susceptible to SSC. (See 3.67 and API 582.)

c) NH_4HS rapidly corrodes admiralty brass tubes and other copper alloys.

3.5.3 Critical Factors

a) NH_4HS concentration, H_2S partial pressure, velocity (i.e. wall shear stress), and/or localized turbulence, pH, temperature, alloy composition, and flow distribution are all critical factors to consider.

b) Corrosion increases with increasing NH_4HS concentration and increasing velocity (i.e. wall shear stress). For carbon steel, solutions below 2 wt % NH_4HS are not generally corrosive. Above 2 wt %, solutions are increasingly corrosive.

c) In hydroprocessing reactors, nitrogen in the feed is converted to ammonia and reacts with H_2S to form NH_4HS. NH_4HS precipitates out of the gas phase in the reactor effluent stream when temperatures drop to within the range of 120 °F to 150 °F (50 °C to 65 °C), depending on the concentration of NH_3 and H_2S, and may cause fouling and plugging unless flushed away with wash water. A similar reaction between NH_3 and H_2S occurs in FCC and coker units, leading to precipitation in the associated fractionator overheads.

d) NH_4HS salt deposits can lead to under-deposit corrosion and fouling. The salts are not corrosive unless they become hydrated at which point they become corrosive.

e) Oxygen and iron in the wash water injected into hydroprocessing reactor effluent can lead to increased corrosion and fouling.

f) The presence of cyanides increases the severity of corrosion in FCC gas plants, coker gas plants, and sour water stripper (SWS) overheads by diminishing the protection afforded by the normally protective sulfide film.

3.5.4 Affected Units or Equipment

a) Hydroprocessing units.

1. Several major failures have occurred in hydroprocessing reactor effluent systems due to localized corrosion.

2. Fouling and/or velocity accelerated corrosion may be found at:

— air cooler header boxes;

- inlet and outlet piping of air coolers;
- exchanger tubes, especially at the inlet and outlet;
- effluent separators and piping into and out of the reactor effluent separators;
- SW draw piping from reactor effluent separators, especially downstream of control valves where flashing may cause severe erosion-corrosion (Figure 3-5-1);
- vapor lines from the high-pressure separator due to entrained or condensed SW;
- hydrocarbon lines from reactor effluent separators due to entrained SW; and
- stripper column overheads containing SW.

b) FCC units.

NH_4HS concentrations are usually less than 2 wt %, but high velocities and/or the presence of cyanides can damage protective iron sulfide scales.

c) SWSs.

High concentrations of NH_4HS and the possible presence of cyanides can lead to corrosion in stripper overhead piping, condensers, and accumulator and reflux piping.

d) Amine units.

High concentrations of NH_4HS may be found in regenerator overheads and reflux piping depending on unit operation.

e) Delayed cokers.

High concentrations of NH_4HS may be found in the gas concentration plant downstream of the fractionator tower.

3.5.5 Appearance or Morphology of Damage

a) General loss in thickness of carbon steel, with the potential for extremely high localized rates of wall loss at changes in direction or turbulent flow areas above 2 wt % concentration. Generalized corrosion, especially if combined with high unit pressure, can lead to rupture failure.

b) High localized corrosion rates have also been seen in straight runs of piping, so locating the site of the worst corrosion can be a challenge.

c) Low velocities may result in extremely localized under-deposit corrosion if sufficient water is not available to dissolve the NH_4HS salts that precipitated.

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

3.5.6 Prevention/Mitigation

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

b) Carefully review design and localized velocities as process conditions change, particularly as NH_4HS concentrations exceed 2 wt % and begin to approach 8 wt % or higher.

c) Use resistant materials of construction (e.g. duplex stainless steel, Alloy 825) at velocities above 20 fps (6 m/s), depending on NH_4HS concentration.

d) Properly design and maintain water wash injection with low oxygen content; provide sufficient excess water to ensure that an adequate amount of water remains as liquid to dilute the NH_4HS salts. Use proper injection spray nozzles and metallurgy.

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

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

3.5.7 Inspection and Monitoring

a) Ammonium bisulfide corrosion can be highly localized and difficult to locate.

b) Determine ammonium bisulfide content through sampling or calculation.

c) UT scanning and/or RT thickness measurement should focus on areas of turbulence and areas of high and low velocity.

1. Special attention should be given to water injection locations in areas of expected water impact (injection point inspection).

2. UT downstream of control valves that see high NH_4HS concentrations.

d) Permanently mounted thickness monitoring sensors can be used.

e) Guided wave testing (GWT) can be used as a screening tool.

f) For steel (magnetic material) air cooler tubes (which are normally finned), internal rotating inspection system (IRIS), magnetic flux leakage (MFL), near-field testing (NFT), and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material air cooler tubes.

g) For steel (magnetic material) exchanger bundle tubes, IRIS, MFL, remote field testing (RFT), and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material exchanger bundle tubes.

h) Water injection facilities and flow meters should be monitored to ensure proper operation. Spray nozzles should be inspected for proper distribution pattern and evidence of damage or distortion.

3.5.8 Related Mechanisms

Erosion/erosion-corrosion (3.27), ammonium chloride corrosion (3.6), concentration cell corrosion (3.19), titanium hydriding (3.66), and chloride SCC (Cl^- SCC) (3.17).

3.5.9 References

1. R.L. Piehl, “Survey of Corrosion in Hydrocracker Effluent Air Coolers,” *Materials Protection*, NACE International, Houston, TX, 1976.

2. E.F. Ehmke, “Corrosion Correlation with Ammonia and Hydrogen Sulfide in Air Coolers,” *Materials Protection*, NACE International, Houston, TX, 1975.

3. J. Turner, “Control Corrosion in Washwater Systems,” *Hydrocarbon Processing*, June 1997, pp. 87–95.

4. C. Harvey and A. Singh, “Mitigate Failures for Reactor Effluent Air Coolers,” *Hydrocarbon Processing*, October 1999, pp. 59–72.

5. C.A. Shargay and G.E. Jacobs “Ammonium Salt Corrosion in Hydrotreating Unit Stripper Column Overhead Systems,” Paper No. 392, *Corrosion/99*, NACE International, Houston, TX.

6. NACE Publication 34101, *Refinery Injection and Process Mixing Points*, NACE International, Houston, TX, March 2001.

7. API Recommended Practice 932-B, *Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems*, American Petroleum Institute, Washington, DC.

8. C. Shargay and S. Marciniec, "Analyzing Water Washing Requirements for Low Severity Hydroprocessing Units," Paper No. 04646, *Corrosion 2004*, NACE International, Houston, TX.

9. R.J. Horvath, M.S. Cayard, and R.D. Kane, "Prediction and Assessment of Ammonium Bisulfide Corrosion Under Refinery Sour Water Service Conditions," Paper No. 06576, *Corrosion/2006*, NACE International, Houston, TX.

10. H. Iwawaki and K. Toba, "Corrosion Behavior of Steels in Concentrated NH_4HS Environments," Paper No. 07576, *Corrosion 2007*, NACE International, Houston, TX.

11. R.J. Horvath et al., "Prediction and Assessment of Ammonium Bisulfide Corrosion Under Refinery Sour Water Service Conditions—Part 2," Paper No. 10349, *Corrosion/2010*, NACE International, Houston, TX.

12. S. Srinivasan, R.J. Horvath, K.M. Yap, and R.D. Kane, "Prediction and Assessment of Ammonium Bisulfide Corrosion Under Refinery Sour Water Service Conditions—Part 3," Paper No. 08929, *Corrosion/2017*, NACE International, Houston, TX.

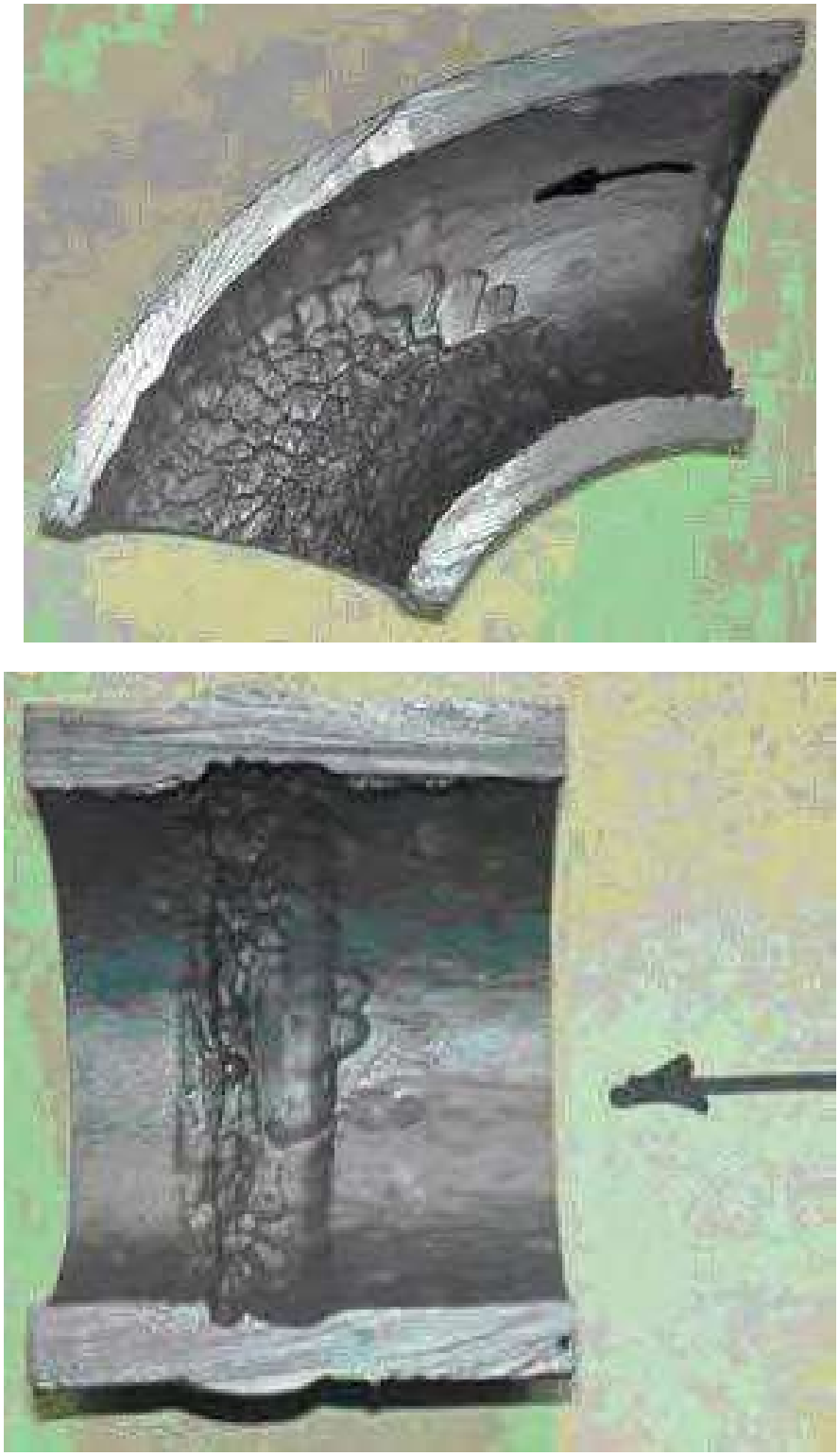


Figure 3-5-1—Ammonium bisulfide corrosion in a 2-in. CS elbow and straight section in a SW line off the cold high-pressure separator (HPS) in an HDT unit.

3.6 Ammonium Chloride and Amine Hydrochloride Corrosion

3.6.1 Description of Damage

Localized corrosion, often pitting, normally occurring under ammonium chloride or amine salt deposits, often in the absence of a free water phase.

3.6.2 Affected Materials

All commonly used materials are susceptible. In order of increasing resistance: carbon steel and low-alloy steels; 300 series SS; duplex stainless steel and Alloys 400, 800, and 825; Alloys 625 and C276; and titanium.

3.6.3 Critical Factors

a) Concentrations of NH_3, hydrochloric acid (HCl), and amine salts; temperature; and water availability are the critical factors.

b) Ammonium chloride salts may precipitate from high-temperature streams as they are cooled, depending upon the concentration of NH_3 and HCl, and may corrode piping and equipment at temperatures well above the water dew point. Salting has been observed up to approximately 400 °F (205 °C).

c) Ammonium chloride salts are hygroscopic and readily absorb water. A small amount of water can lead to very aggressive corrosion [>100 mpy (>2.5 mm/yr)].

d) Ammonium chloride is highly water soluble, highly corrosive, and forms an acidic solution when mixed with water. Neutralizing amines can also react with hydrogen chloride to form amine hydrochlorides that can act in a similar fashion.

e) Corrosion rates increase with increasing temperature.

f) When the salts deposit above the water dew point, a water wash injection may be required to dissolve them.

3.6.4 Affected Units or Equipment

a) Crude tower overheads.

1. Tower top, top trays, and overhead piping and exchangers may be subject to fouling and corrosion. Deposits may occur in low-flow zones due to ammonia and/or amine chloride salts condensing from the vapor phase.

2. Top pumparound streams may be affected if ammonia or amine chloride salts are present.

b) Hydroprocessing.

1. Reactor effluent streams are subject to ammonium chloride salt fouling and corrosion. Water washing may be required if exchanger fouling or loss in duty occurs.

c) Catalytic reforming.

d) Reactor effluent streams and the H_2 recycle system are subject to ammonium chloride salting and corrosion.

e) FCC unit and coker fractionator overheads.

1. Overhead systems and top pumparounds are subject to ammonium chloride corrosion and salting.

3.6.5 Appearance or Morphology of Damage

a) The salts have a whitish, greenish, or brownish appearance. Water washing and/or steam out will remove deposits so that evidence of fouling may not be evident during an internal VT.

b) Corrosion underneath the salts is typically very localized and can result in pitting.

c) Corrosion rates can be extremely high.

3.6.6 Prevention/Mitigation

Alloys that are more pitting resistant will have improved resistance to ammonium chloride salts, but even the most corrosion-resistant nickel-based alloys and titanium alloys may suffer pitting corrosion.

a) Crude unit.

1. Limit salts by limiting chlorides in the tower feed through desalting and/or the addition of caustic to the desalted crude.

2. A water wash may be required in the crude tower overhead line to flush the salt deposits.

3. Filming amine inhibitors are often added to control corrosion but may not reach metal surfaces under deposits that have already formed.

b) Hydroprocessing.

1. Limit chlorides in the hydrocarbon feed to the reactor.

2. Limit chlorides in the make-up hydrogen supply.

3. A continuous or intermittent water wash may be required in the reactor effluent stream to flush out the salt deposits or, preferably, prevent them from forming.

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

c) Catalytic reforming.

1. Net hydrogen produced can be treated in alumina bed chloride traps to remove chlorides.

2. Water washing has been used in some cases, but the system must be carefully designed.

3. Some tower overheads may require neutralizing or filming amines.

d) FCC and coker units.

1. Continuous water wash in overheads is usually used to dissolve salts as they form.

2. Intermittent water wash can be used to remove salt deposits from fractionator trays. This usually requires “slumping” the column and re-running of affected cuts.

3.6.7 Inspection and Monitoring

a) Ammonium chloride corrosion can be highly localized and difficult to locate. Salts are often mobile, depending on size of accumulation and hydration, causing them to flow with hydraulic traffic and gravity.

b) RT or UT scanning methods [automated ultrasonic testing (AUT), manual close-grid, scanning UT] can be used to determine remaining wall thickness. These methods are preferred over typical spot UT thickness monitoring because the corrosion is so highly localized.

c) GWT can be used as a screening tool.

d) Permanently mounted thickness monitoring sensors can be used.

e) Water injection facilities and flow meters should be monitored to ensure proper operation. Spray nozzles should be inspected for proper distribution pattern and evidence of distortion or other damage.

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

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

h) For steel (magnetic material) air cooler tubes (which are normally finned), IRIS, MFL, NFT, and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material air cooler tubes.

i) For steel (magnetic material) exchanger bundle tubes, IRIS, MFL, RFT, and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material exchanger bundle tubes.

3.6.8 Related Mechanisms

Hydrochloric acid corrosion (3.37), Cl^- SCC (3.17), aqueous organic acid corrosion (3.7), and concentration cell corrosion (3.19).

3.6.9 References

1. C. Shargay et al., “Design Considerations to Minimize Ammonium Chloride Corrosion in Hydrotreater REACs,” Paper No. 1543, *Corrosion/2001*, NACE International, Houston, TX.

2. C. Shargay et al., “Ammonium Salt Corrosion in Hydrotreating Unit Stripper Column Overhead Systems,” Paper No. 392, *Corrosion/99*, NACE International, Houston, TX.

3. NACE Publication 34101, *Refinery Injection and Process Mixing Points*, NACE International, Houston, TX, March 2001.

4. J. Turner, “Control Corrosion in Washwater Systems,” *Hydrocarbon Processing*, June 1997, pp. 87–95.

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

6. NACE Publication 34109, *Crude Distillation Unit—Distillation Tower Overhead System Corrosion*, NACE International, Houston, TX, 2009.

7. API Recommended Practice 932-B, *Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems*, American Petroleum Institute, Washington, DC.

3.7 Aqueous Organic Acid Corrosion

3.7.1 Description of Damage

Organic compounds present in some crude oils decompose in the crude furnace to form low molecular weight organic acids (Table 3-7-1) that are soluble in water. They may also result from additives used in upstream operations or desalting. These acids can contribute significantly to aqueous corrosion depending on the type and quantity of acids and the presence of other contaminants, particularly if they condense in distillation tower overhead systems. They can also cause corrosion at mix points where recovered oil streams are injected.

3.7.2 Affected Materials

a) Carbon steel and low-alloy steels are affected.

b) Most corrosion-resistant alloys used in crude tower overhead systems are generally not affected.

1. Austenitic stainless steels are generally resistant, but this mechanism is often associated with streams that cause inorganic acid corrosion as well as pitting and SCC due to halogens (e.g. chlorides), so their use should be avoided unless it is known that halogens are not present.

3.7.3 Critical Factors

a) Corrosion is a function of the type and quantity of organic acids, metal temperature, fluid velocity, system pH, and presence of other acids.

b) The low-molecular-weight organic acids that are formed include formic acid, acetic acid, propionic acid, and butyric acid.

c) The lower-molecular-weight acids such as formic acid and acetic acid are the most corrosive. They are soluble in naphtha and are extracted into the water phase, once the water condenses, and contribute to a reduction of pH.

d) The presence of organic acids will contribute to the overall demand for neutralizing chemicals, but their effects may be completely masked by the presence of other acids such as HCl, H_2S, carbonic acid, and others.

e) Corrosion is most likely to be a problem where relatively “non-corrosive” conditions have existed in an overhead system. When there is a sudden increase in low molecular weight organic acids, it can reduce the pH of the water in the overhead system and cause a potentially unexpected increase in neutralizer demand.

f) The type and quantity of organic acids formed in the overhead system are crude specific. One source of these acids is believed to be the thermal decomposition of naphthenic acids in the crude, which may be precursors to light organic acid formation. In that case, the processing of higher total acid number (TAN) crudes might increase organic acid in the overheads. However, very little published information is available on this subject.

g) Some higher molecular weight organic acids condense above the water dew point in overhead systems, but they are generally not present in sufficient quantities to cause corrosion.

h) Light organic acids such as acetic acid are sometimes added during oilfield operations, e.g. in dehydrators or desalters to improve performance and inhibit calcium naphthenate salt deposition. (Reference 2) Such acids will vaporize in the crude preheat exchangers and furnace and go up the column into the crude tower overhead system.

i) Other, high molecular weight acids used as oilfield additives can thermally decompose at crude unit temperatures to form volatile, corrosive light organic acids such as acetic and formic acids.

j) In general, light organic acids do not generate the severity of corrosion associated with inorganic acids such as HCl. Table 3-7-1 shows the HCl equivalent factor for corrosion by organic acids in overhead systems. To calculate the HCl equivalent of an organic acid, multiply the content of the organic acid (in weight ppm) by the factor for that acid, and the result will be the equivalent content of HCl (in ppmw). This number can then be used to estimate the additional neutralizer needed in the overhead system to compensate for the organic acids present. This must be done with caution, because excess neutralizer can lead to amine hydrochloride salts in overhead systems.

3.7.4 Affected Units or Equipment

a) All carbon steel piping and process equipment in crude tower, vacuum tower, visbreaker, and coker fractionator overhead systems including heat exchangers, towers, and drums are susceptible to corrosion where acidic conditions occur.

b) Localized corrosion can occur at mix points from recovered oil streams when wet streams combine with streams contaminated with organic acid.

c) Corrosion tends to occur where water accumulates or where hydrocarbon flow directs water droplets against metal surfaces. Examples include the bottoms of overhead separator drums and exchanger shells or channels, the boots of separator drums, and liquid hold-up areas on trays.

d) In horizontal piping, organic acid corrosion is generally found both in the vapor space where liquid water can condense and along the bottom of the piping where liquid water may run.

e) Corrosion is also sensitive to flow rate and will tend to be more severe in higher-velocity and turbulent areas in piping systems such as elbows, tees, downstream of pumps, and downstream of control valves. Other areas of potentially more severe corrosion due to velocity and turbulence include overhead transfer lines, overhead condensers and separator drums, and exchanger tubes.

3.7.5 Appearance or Morphology of Damage

a) Aqueous organic acid corrosion will result in thinning. General and local wall loss can be expected. In carbon steels, local losses are observed where a water phase is being formed such as during condensation or separation.

b) Light organic acid corrosion typically leaves the corroded surface smooth and damage may be difficult to distinguish from corrosion by other acids in the overhead system. It is sometimes mistaken for HCl corrosion or carbonic acid (CO_2) corrosion.

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

d) Localized pitting occurs in low-velocity or condensing conditions.

3.7.6 Prevention/Mitigation

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

b) The TAN of the crudes being processed can be used as an initial guide to determine the neutralizer requirement. If the crude TAN increases, one should anticipate an increase in the acid concentration in the overhead system.

c) After a new crude is processed, a review of analyses of water samples from the boot of the overhead separator drum can be used to determine how much light organic acid reaches the overhead system and thereby optimize future neutralizer additions.

d) Filming amines can also be used to prevent corrosion if the filming amine selected does not react with the organic acid. However, filming amines are generally not as effective as neutralization in mitigating overhead system corrosion.

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

3.7.7 Inspection and Monitoring

a) Various UT and RT techniques can be used to assess metal loss.

b) GWT and electromagnetic acoustic transducer (EMAT) can be utilized to screen for wall loss.

c) Corrosion probes and corrosion coupons have proven valuable, especially in conjunction with water sample analysis.

d) Permanently mounted thickness monitoring sensors can be used.

e) Infrared thermography scanning can also be used to detect locations where liquid water may exist and in this way supplement other NDE methods.

f) The pH should be monitored where water is known to accumulate in the process, particularly at the overhead accumulation drum of the crude tower. If a low pH is found that cannot be accounted for by the level of chlorides measured, additional acids, potentially including organic acids, are likely present.

3.7.8 Related Mechanisms

HCl corrosion (3.37) and naphthenic acid corrosion (NAC) (3.46).

3.7.9 References

1. R.R. Petersen, “Improve Corrosion Control by Computer Simulation,” *Hydrocarbon Processing*, January 1992, pp. 50–55.

2. S. Kapusta, F. van den Berg, R. Daane, and M.C. Place, “The Impact of Oil Field Chemicals on Refinery Corrosion Problems,” Paper No. 03649, *Corrosion/2003*, NACE International, Houston, TX.

3. S. Lordo, J.M. Garcia, and S. Garcia-Swofford, “Desalter Acidification Additives and Their Potential Impacts on Crude Units,” Paper No. 08556, *Corrosion/2008*, NACE International, Houston, TX.

4. R. Sharpe et al., “Crude Unit Overhead Corrosion Control,” Paper No. 98585, *Corrosion/98*, NACE International, Houston, TX.

5. NACE Publication 34109, *Crude Distillation Unit—Distillation Tower Overhead System Corrosion*, NACE International, Houston, TX, 2009.

6. J.R. Rue and D.P. Naeger, “Advances in Crude Unit Corrosion Control,” Paper No. 87199, *Corrosion/87*, NACE International, Houston, TX.

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

Table 3-7-1—Light Organic Acid Corrosion Equivalency Factors

Acid	HCl Equivalent Factor
Formic	0.76
Acetic	0.61
Propionic	0.49
Methyl propionic	0.41
Butanoic	0.41
3-methyl butanoic	0.36
Pentanoic	0.36
Hexanoic	0.31
Heptanoic	0.28

3.8 Atmospheric Corrosion

3.8.1 Description of Damage

Corrosion that occurs from moisture associated with atmospheric conditions. Marine environments and moist, polluted industrial environments with airborne contaminants are the most severe. Dry rural environments cause very little corrosion.

3.8.2 Affected Materials

Carbon steel, low-alloy steels, and copper alloyed aluminum.

3.8.3 Critical Factors

a) The physical location of the plant (industrial, marine, urban, rural).

b) The amount of moisture (humidity, rainfall) typically present or the presence of cooling tower mist.

c) The presence of salts, sulfur compounds, dirt, or other contaminants in the air.

d) Chlorides, H_2S, fly ash, and other airborne contaminants from cooling tower and wet gas scrubber drift, furnace stacks, and other equipment accelerate corrosion.

e) Orientation to the prevailing wind and rain.

f) Corrosion rates increase with temperature up to about 250 °F (120 °C). Above 250 °F (120 °C), surfaces are usually too dry for corrosion to occur except under insulation. (See 3.22.)

g) Designs that trap water or moisture in crevices or other configurations are more prone to attack.

h) Marine environments can be very corrosive (about 20 mpy) as are industrial environments that contain acids or sulfur compounds that can form acids (about 5 mpy to 10 mpy).

i) Inland locations exposed to a moderate amount of precipitation or humidity are considered moderately corrosive environments (about 1 mpy to 3 mpy).

j) Dry rural environments usually have very low corrosion rates (<1 mpy).

k) Bird droppings can also cause accelerated corrosion and unsightly stains.

3.8.4 Affected Units or Equipment

a) Unpainted, uninsulated carbon steel and low-alloy steel piping and equipment operating below 250 °F (120 °C) where moisture can contact the surface.

b) Uninsulated carbon and low-alloy steel equipment with deteriorated paint/coating.

c) Equipment downwind of cooling towers and wet gas scrubbers.

d) Equipment may be susceptible if cycled between ambient and higher or lower operating temperatures.

e) Equipment shut down or idled for prolonged periods unless properly mothballed.

f) Tanks and piping are particularly susceptible. Piping that rests on pipe supports is very prone to attack due to water entrapment between the pipe and the support.

g) Piers and docks are very prone to attack from the marine environment.

h) Bimetallic connections such as copper to aluminum electrical connections.

3.8.5 Appearance or Morphology of Damage

a) The attack will be general or localized, depending upon the condition of the coating, if any, and whether or not the moisture is trapped.

b) If there is no coating, corrosion or loss in thickness can be more general and widespread.

c) Localized coating failures will promote localized corrosion.

d) Metal loss may not be visually evident, although normally a distinctive iron oxide (red rust) scale forms as shown in Figure 3-8-1.

3.8.6 Prevention/Mitigation

Paints or coatings are normally applied to otherwise unprotected equipment to prevent atmospheric corrosion. Surface preparation and proper coating application are critical for long-term protection in corrosive environments.

3.8.7 Inspection and Monitoring

a) VT includes direct/line-of-sight and indirect methods using a camera, mirror, laser scanning, and/or structured white light imaging with pit gages.

b) UT can include techniques like straight beam or angle beam (SWUT or PAUT) to directly measure remaining wall thickness or screening techniques using EMAT or GWT.

c) RT may include traditional (film based), digital, or computed radiography media and may incorporate techniques such as contact or profile RT as well as open system imaging.

d) ECT may include a screening technique such as pulsed eddy current (PEC).

3.8.8 Related Mechanisms

Corrosion under insulation (CUI) (3.22) and concentration cell (touch point) corrosion (3.19).

3.8.9 References

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

Figure 3-8-1—Atmospheric corrosion of an LPG line in close proximity to a cooling tower.

3.9 Boiler Water and Steam Condensate Corrosion

3.9.1 Description of Damage

General corrosion and pitting in the boiler system and condensate return system. It is primarily the result of dissolved oxygen and/or carbon dioxide, which could lead to oxygen pitting corrosion and carbonic acid corrosion, respectively. Flow accelerated corrosion (FAC) in these systems may occur either as general wall thinning corrosion or localized corrosion at high velocity, high turbulence, or change of flow direction locations.

3.9.2 Affected Materials

Carbon steel and low-alloy steels.

3.9.3 Critical Factors

a) Critical factors are the concentration of dissolved gas (oxygen and/or carbon dioxide), pH, temperature, quality of the feedwater, and the specific feedwater treating system.

b) Corrosion protection in the boiler is accomplished by laying down and continuously maintaining a layer of protective Fe_3O_4 (magnetite).

c) In the case of FAC, this protective oxide layer is dissolved or prevented from forming. Carbon steel is the most affected. Alloying elements in low-alloy steels such as Cr, Cu, and Mo can enhance corrosion resistance. The most critical temperature for FAC is 300 °F (150 °C), and it decreases with increasing pH. Too low an oxygen concentration increases the corrosion due to the inability to form the protective oxide layer. At least 3 ppb to 7 ppb may be required to form the oxide layer.

d) The chemical treatment for scale and deposit control must be adjusted to coordinate with the oxygen scavenger for the specific water service and BFW treating system.

e) Oxygen pitting can occur if the deaeration and oxygen scavenging treatment are not working correctly.

3.9.4 Affected Units or Equipment

a) Corrosion can occur throughout the boiler water treatment system, including the deaerating equipment, feedwater lines, and pumps, as well as in the steam generation system including stage heaters, economizers, and boiler tubes as well as process unit steam generators.

b) Corrosion in the condensate return system as well as in process unit reboilers and associated piping may be due to carbon dioxide, although oxygen pitting from oxygen contamination is also possible as well as FAC if the proper conditions are present.

c) Threaded connections are especially susceptible.

3.9.5 Appearance or Morphology of Damage

a) Corrosion from oxygen is normally a pitting type damage. It can occur anywhere in the system there is in-leakage of air or even if only very small quantities break through the oxygen scavenging treatment. Oxygen is particularly aggressive in equipment such as closed heaters and economizers where there is a rapid water temperature rise. (Figure 3-9-1)

b) Carbon dioxide corrosion is normally smooth, but it can also cause grooving of the pipe wall. (Figure 3-9-2)

c) Corrosion may be localized at areas where gases in the water are most concentrated, such as at the water to vapor interface level in a vertical reboiler.

d) FAC failures are often located in areas where there is a flow disturbance such as an orifice run, flow meter, elbow, reducer, or other types of fittings. The wall thinning occurs just downstream of these flow disturbances,

leaving behind a corroded surface free of oxide scale, sometimes with a specific flow pattern. FAC has led to rupture of piping.

3.9.6 Prevention/Mitigation

a) Oxygen removal from BFW typically includes mechanical deaeration followed by scavenging with catalyzed sodium sulfite or hydrazine, depending on the system pressure level. Proper deaerator operation and accurately controlled scavenger chemical addition are important. A residual of the oxygen scavenger is carried into the steam generation system to handle any oxygen ingress beyond the deaerator.

b) If the scale and deposit control along with the magnetite maintenance treatment scheme do not minimize carbon dioxide corrosion in the condensate return system, an amine inhibitor treatment might be required.

c) Boiler water needs to be blown down to control the concentration of solids and non-condensable gases. Steam equipment should be checked to ensure there are working non-condensable vents. It is also important that steam piping and equipment allow for blowdown of condensation (e.g. using steam traps and functional mechanical steam separation devices like coalescers).

d) Water treatment, sampling, and analysis are the common methods used to ensure integrity and prevent boiler water and condensate corrosion.

    1. It may be necessary to modify or improve the water treatment program if problems such as a ruptured boiler tube or condensate leaks occur in the boiler water or condensate systems.

e) The pH, temperature, and oxygen concentration are the main parameters that can affect the potential for FAC. BFW pH from 9.2 to 9.6 is often recommended. Upgrading the material to Cr-Mo steel usually solves the problem.

    1. Too low or total absence of oxygen is no longer considered the best corrosion control for BFW and condensate. Oxygenated treatments that deliberately inject oxygen into the condensate and BFW system or the use of oxygen scavenger at reduced concentrations may be necessary to maintain oxygen levels within the desired range to mitigate FAC.

3.9.7 Inspection and Monitoring

a) Monitoring the appropriate parameters can indicate whether the treatment program is performing satisfactorily.

    1. Parameters that can be monitored through analysis include pH, alkalinity, hardness, conductivity, chlorine or residual biocide, dissolved gases (oxygen and carbon dioxide), iron, copper, and total dissolved solids

b) Vacuum testing can be used to check for air ingress into the condenser hotwell.

c) UT and RT methods can be used to monitor for pipe wall thinning.

d) For boilers, there are no practical online inspection methods.

    1. UT and RT can be performed on boiler tubes and other boiler components when the system is offline.

3.9.8 Related Mechanisms

CO_2 corrosion (3.18), corrosion fatigue (3.21), erosion/erosion-corrosion (3.27), oxygenated water corrosion (3.49), and ammonia SCC of copper alloys (3.4).

3.9.9 References

1. *Betz Handbook of Industrial Water Conditioning*, Eighth Edition, Betz Laboratories, Trevose, PA, 1980.

2. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991.

3. NACE SP0590, *Prevention, Detection, and Correction of Deaerator Cracking*, NACE International, Houston, TX.

4. T.Y. Chen et al., "Condensate Corrosion in Steam Generating Systems," Paper No. 98718, *Corrosion/98*, NACE International, Houston, TX.

5. R.B. Dooley and V.K. Chexal, "Flow-accelerated Corrosion," Paper No. 99347, *Corrosion/99*, NACE International, Houston, TX.

6. Nuclear Safety NEW/CSNI/R(2014), CODAP Topical Report: "Flow Accelerated Corrosion (FAC) of Carbon Steel and Low Alloy Steel Piping in Commercial Nuclear Power Plants," https://www.oecd-nea.org/nsd/docs/2014/csni-r2014-6.pdf, June 2014.

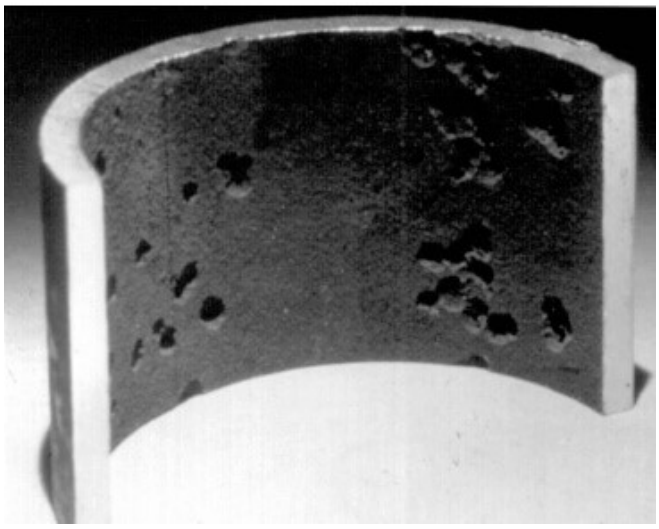


Figure 3-9-1—Pits caused by oxygen corrosion.

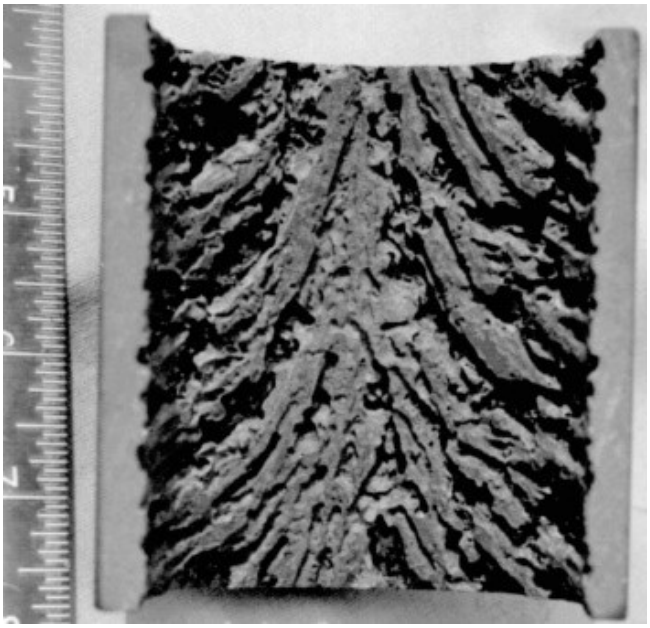


Figure 3-9-2—Jagged fir-tree pattern of corrosion inside a tilted steel pipe caused by condensing steam containing high concentrations of carbon dioxide.

3.10 Brine Corrosion

3.10.1 Description of Damage

a) Widespread or localized pitting occurring on the surface of equipment exposed to aqueous solutions of dissolved salts, typically a chloride or other halide salt. This mechanism is often present with other mechanisms such as oxygen corrosion, galvanic corrosion, and microbiologically influenced corrosion (MIC).

b) In chloride brine corrosion of stainless steels, pits are initiated where chlorides break down the passive layer. Once the pit is initiated, chlorides migrate within the pit, hydrolyze to an acidic species, decrease the pH in the pit, and further accelerate corrosion by this autocatalytic process. A similar process occurs in crevices. Additionally, other anions like nitrates and sulfates hydrolyze within pits and crevices to drive the pH down, but these are less mobile than chlorides so their effect is less significant.

3.10.2 Affected Materials

a) Carbon steel, alloy steel, or stainless steel, with carbon steel being the most common material exposed to brine solutions. Aluminum alloys are also susceptible to brine corrosion. Ni-Cr-Mo alloys have improved resistance to brine corrosion.

b) Copper alloys are generally more resistant to pitting in brine solutions than stainless steel and carbon steel, but the tenacity of the protective film is affected by other contaminants in the stream, including sulfides and ammonia.

c) Resistance of specific alloys is complicated by other concurrent damage mechanisms. For example, oxygen corrosion or under deposit corrosion can be active, with the brine solution chemistry contributing to these mechanisms.

d) Fiber reinforced plastic (FRP) piping is immune to this damage mechanism.

3.10.3 Critical Factors

a) Concentration of dissolved salt, oxygen concentration, pH, velocity, and temperature are the critical factors.

b) Corrosion rates increase with increasing temperature.

c) Corrosion rates increase with increasing oxygen content.

d) Corrosion rates typically increase with decreasing pH, the corrosion becoming more aggressive in more acidic solutions. Decreasing pH also increases pitting and crevice corrosion rates of stainless steels due to the passive layer being less stable at lower pH.

e) Corrosion rates increase with increasing salt content. For stainless steels and related alloys, increasing concentration of halides reduces the critical pitting temperature and critical crevice corrosion temperature for a given alloy.

f) The type of salt species present will affect the corrosion rate. Chlorides are the most common cause of corrosion in brine solutions, but other halides, e.g., bromides can also cause corrosion. Chlorides, sulfates, and nitrates contribute to oxygen corrosion of carbon steel by migrating into oxygen corrosion pits, hydrolyzing to form acidic ions, and decreasing the pH under a tubercle.

g) High velocity can contribute to erosion-corrosion, especially if particulates are present. However, stagnant conditions can also exacerbate corrosion by allowing accumulation of deposits. Copper-alloys and carbon steel tend to be more susceptible to erosion-corrosion than stainless steel.

h) The chloride pitting and crevice corrosion resistance of stainless steels and higher alloy Fe-Ni-Cr alloys is quantified by the Pitting Resistance Equivalent Number (PREN).

1. PREN = %Cr + 3.3 x (%Mo + 0.5 x %W) + 16 x %N

2. Generally, a PREN of 40 or higher is considered necessary to resist corrosion in aerated seawater in ambient conditions. In stainless steels, an increase in molybdenum content improves resistance to chloride pitting and crevice corrosion in brine solutions, as can be seen by the increase in PREN. Nitrogen additions are also very potent in increasing resistance.

3. Chloride pitting penetration rates can be worse in stainless steels with a low PREN than in carbon steel due to the cathodic potential provided by the passive layer around the pit in driving the pitting corrosion process as well as the nature of the autocatalytic acid chloride hydrolysis mechanism of chloride pitting in stainless steel.

i) The presence of free chlorine above approximately 0.5 ppm (e.g. biocide treatment in seawater systems) increases seawater corrosion rates of carbon steel and stainless steel, in both stagnant and flowing conditions.

j) The presence of sulfur-containing compounds can reduce the corrosion resistance of copper-based alloys by changing the passivity of the protective surface film.

k) The presence of hydrogen sulfide can accelerate attack. H2S ionizes in the brine solution to form an acid that reacts with steel to form loose, porous, non-protective iron sulfide deposits on the pipe surface.

l) The use of free-machining stainless steel can initiate pitting more rapidly.

3.10.4 Affected Units or Equipment

a) Crude distillation unit desalters and desalter effluent systems.

b) Effluent water treatment systems. High corrosion rates are commonly observed in transfer lines between ponds, outlet piping of brine separators, and piping in intermittent service. (Figures 3-10-1 and 3-10-2)

c) Salt driers for water removal from final product.

d) Seawater systems (e.g. firewater).

e) Water softener regeneration systems.

3.10.5 Appearance or Morphology of Damage

a) Carbon Steel - Heavy scaling and possible tubercles since the mechanism is typically a result of chlorides or other anions accelerating oxygen pitting. Removal of the scale reveals under-deposit type corrosion and large, wide pits, with corrosion rates observed up to 60 mpy.

1. Where sulfate reducing bacteria (SRB) are present, severe pitting/channeling can occur along the top or bottom of the pipe.

2. Preferential corrosion in welds and heat affected zones sometimes occurs in carbon steel.

b) Stainless Steel – Sharp, deep, isolated pits are typical of chloride pitting and crevice corrosion of stainless steel. Chloride SCC is also possible, depending on the temperature. (See 3.17.)

3.10.6 Prevention/Mitigation

a) Sources of dissolved oxygen should be identified and eliminated. A deaerated water source should be used for desalter wash water make-up. Accidental aeration can be corrected through improved design or water treatments such as vacuum deaeration or chemical scavenging. An effective scavenger in brine systems is sodium metabisulfite. Water is oxygenated during movement in and out of ponds, especially where it freefalls. O2 content should be checked downstream of the brine separator and discharge of pumps.

b) Heat exchangers should be operated to prevent vaporization or precipitation of deposits.

c) Low residual chlorine levels should be maintained when treating for prevention of MIC (< 0.5 ppm for carbon steel, 0.7-5 ppm for super duplex systems depending on temperature, and < 5 ppm for Cu-Ni). Bacteria which can contribute to microbiologically influenced corrosion should be monitored. (See 3.45.) Typical locations to monitor for SRB are inlets and outlets to fresh water rivers, canals, or ponds.

d) Upgrading to a more corrosion resistant alloy such as a Ni-Cr-Mo alloy or to a non-metallic such as FRP or polyvinyl chloride (PVC) can help mitigate corrosion. FRP is immune and has been the modern material of choice. However, there are limitations on operating pressures and temperatures that can impact the ability to meet design and cost constraints.

e) Internal coatings can provide some protection to carbon steel for this type of service. Epoxy phenolic and coal tar epoxy coatings have been used as well as polypropylene-lined pipe. However, care must be taken to avoid galvanic coupling with more noble materials. (See 3.31.) Also, the coating integrity must be well maintained to prevent creating an aeration cell next to voids.

3.10.7 Inspection and Monitoring

a) UT, including UT scanning, can be used for external, opposite side thickness measurements. RT can also be used where pipe dimensions allow.

b) GWT can be used for screening long pipe runs to identify areas for local follow-up measurements, but it may not detect isolated pitting.

c) Corrosion coupons or electric resistance probes can assist in determining short & long-term corrosion rates. The coupons also provide a visual indication of the damage mode present in the system.

d) Dissolved O2 content should be monitored.

e) Permanently-mounted thickness monitoring sensors can be used.

3.10.8 Related Mechanisms

Microbiologically influenced corrosion (3.45), erosion/erosion-corrosion (See 3.27), chloride stress corrosion cracking (See 3.17), cooling water corrosion (3.20), galvanic corrosion (3.31), concentration cell corrosion (3.19), and oxygenated water corrosion (3.49).

3.10.9 References

1. D. A. Jones, “Principles and Prevention of Corrosion,” 2nd edition, Prentice-Hall, Inc, 1996.
2. H. M. Herro, R. D. Port, “The Nalco Guide to Cooling Water System Failure Analysis,” McGraw-Hill Inc, 1993.
3. “Evaluation of In-Line Corrosion Coupons,” R. W Elliot, Ortech Corporation, September 1998. Paper No. 98-J41-M0201.
4. W. Schleich, “Selection of Material for Seawater Piping Systems,” KME Germany AG, Rev. 2008
5. NORSOK Standard M-001, Materials Selection, Rev. 3, Nov. 2002.
6. S. A. Silverman, et. al., “Use of High-Strength Alloys and Elastomers in Heavy Completion Brines,” SPE 84515, SPE Annual Technical Conference and Exhibition in Denver, Colorado, USA, 8 October 2003, Society of Petroleum Engineers, Inc.
7. J. W. Oldfield, G. L. Swales, B. Todd, “Corrosion of Metals in Deaerated Seawater,” Proceedings of the Second BSE-NACE Corrosion Conference, January 19–21, 1981, Bahrain.

Figure 3-10-1 – Brine corrosion at a flange connection.

Figure 3-10-2 – Close-up of brine corrosion on flange in Figure 3-10-1.

3.11 Brittle Fracture

3.11.1 Description of Damage

Brittle fracture is the sudden rapid fracture under stress (residual or applied) where the material exhibits little or no evidence of ductility or plastic deformation. Although rare in refining operations, in-service brittle fracture of a pressure vessel or other pressurized equipment can have serious consequences.

3.11.2 Affected Materials

Carbon steels and low-alloy steels are of prime concern, particularly older steels. 400 series SS are also susceptible even if not embrittled. In addition, materials susceptible to an embrittling mechanism such as sigma phase embrittlement (3.56), 885 °F (475 °C) embrittlement (3.1), temper embrittlement (3.63), strain-aging embrittlement (3.60), or titanium hydriding (3.66) pose a risk for brittle fracture if they are sufficiently embrittled.

3.11.3 Critical Factors

a) Brittle fracture can occur in a potentially susceptible piece of equipment containing a flaw or other significant stress concentrator. Three primary factors are:

   1. the material's fracture toughness (resistance to crack-like flaws) as indicated in a Charpy impact test or other fracture mechanics test;

   2. the size, shape, and stress concentration effect of the flaw; and

   3. the amount of residual and applied stresses on the flaw.

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

c) Steel cleanliness (level of S, P, and other impurity elements) and grain size have a significant influence on toughness and resistance to brittle fracture. In addition, higher-strength, micro-alloyed steels can experience secondary hardening in certain temperature ranges due to the precipitation of embrittling phases that reduce the fracture toughness of the steel. Micro-alloying elements like V, Cb (Nb), B, and Ti in certain ranges as well as S, P, and Mn above their residual limits can cause low toughness.

d) The heat treatment condition of the material can affect its fracture toughness.

e) Thicker material sections have an inherently lower resistance to brittle fracture due to the nature of the stress state within a thick section of metal. Thick sections are under higher constraint (i.e. they are constrained from deforming), which increases triaxial stresses at the crack tip and promotes brittle, rather than ductile, fracture.

f) In most cases, in materials that exhibit a ductile-to-brittle transition, brittle fracture occurs only at temperatures below the Charpy impact transition temperature (also called the ductile-to-brittle transition temperature), the temperature at and below which the toughness of the material drops off sharply.

3.11.4 Affected Units or Equipment

a) Equipment manufactured to the ASME *Boiler and Pressure Vessel Code* (*BPVC*) Section VIII, Division 1, prior to the December 1987 Addenda, had no *Code*-required restrictions on notch toughness for vessels operating at cold temperatures. However, this does not mean that all vessels fabricated prior to this date will be subject to brittle fracture. Many designers, purchasers, and users specified supplemental impact tests on equipment that was intended to be in cold service.

   1. Equipment made to the same code after this date were subject to the requirements of UCS 66 (impact exemption curves), which address impact toughness requirements at low temperatures.

b) Most processes run at elevated temperature, so the main concern is for brittle fracture during start-up, shutdown, or hydrotest/tightness testing. Thick wall equipment in particular in any unit should be evaluated.

c) Brittle fracture resulting from an autorefrigeration event should be considered in units processing light hydrocarbons such as methane (CH_4), ethane/ethylene, propane/propylene, or butane. This includes alkylation units, olefin units, and polymer plants (polyethylene and polypropylene). Storage bullets and spheres for light hydrocarbons may also be susceptible.

d) Brittle fracture can occur during ambient temperature hydrotesting due to high stresses and low toughness at the testing temperature.

3.11.5 Appearance or Morphology of Damage

a) Cracks will typically be straight, non-branching, and largely devoid of any associated plastic deformation, although fine shear lips may be found along the free edge of the fracture, or localized necking around the crack may occur. (Figure 3-11-1 to Figure 3-11-5)

b) The fracture surface, if undamaged after the initial fracture, will exhibit visible “chevron markings” that point back to the crack origin point. These markings can be helpful in locating the initiating cause of the brittle fracture. (Figure 3-11-6)

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

3.11.6 Prevention/Mitigation

a) For most new equipment, brittle fracture is prevented by using materials compliant with UCS 66 in Section VIII of the ASME *BPVC*. In some cases, equipment will need to be specifically designed for low-temperature operation including upset and autorefrigeration events or will have additional requirements to account for a large wall thickness. Materials with controlled chemical composition, special heat treatment, and/or impact test verification may be required.

1. Using fully killed, fine grain steel with austenite grain size finer than 6 (McQuaid Ehn Method) will achieve the desired toughness in many situations.

b) For existing equipment, the combination of stress, material toughness, and existing or potential flaw size govern the probability of a brittle fracture event. In cases where there is a concern for the possibility of a brittle fracture occurring, an engineering evaluation can be performed in accordance with API 579-1/ASME FFS-1, Section 3, Level 1 or 2.

c) Preventing and minimizing the possibility of a brittle fracture in existing equipment rely upon controlling the operating conditions (pressure, temperature), minimizing pressure at ambient temperatures during start-up and shutdown, not hydrotesting at too low a temperature, and periodic inspection at high-stress locations, as applicable to the specific situation. A pressure vessel can also be re-rated to a lower maximum allowable working pressure (MAWP) and resulting new, higher minimum design metal temperature (MDMT), per the requirements of the *National Board Inspection Code*, ASME *BPVC* Section VIII, Division 1, or other jurisdictional requirements or codes.

d) Where brittle fracture is deemed a concern, some reduction in the likelihood of a brittle fracture may be achieved by following API 579-1/ASME FFS-1.

e) In some cases, selecting or changing to a material with good low-temperature toughness, e.g. an appropriate low-temperature ASTM/ASME grade of steel (often containing a few percent of nickel) or an austenitic (300 series) stainless steel, will be necessary to achieve the desired low-temperature fracture toughness.

3.11.7 Inspection and Monitoring

a) Routine inspection is not normally used to detect or mitigate brittle fracture, but awareness of susceptible equipment can help prevent future damage.

b) Susceptible vessels can be inspected for pre-existing crack-like fabrication flaws, as well as for cracking from relevant in-service cracking mechanisms using magnetic particle testing (MT), PT, and/or UT, as applicable.

3.11.8 Related Mechanisms

Temper embrittlement (3.63), strain age embrittlement (3.60), 885 °F (475 °C) embrittlement (3.1), titanium hydriding (3.66), and sigma embrittlement (3.56).

3.11.9 References

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

2. J.A. Smith and S.T. Rolfe, *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 418, Welding Research Council, Shaker Heights, OH.

3. British Standard 7910, *Guide to Methods for Assessing the Acceptability of Flaws in Metallic Structures*, British Standards Institution, London, UK.

4. ASME *Boiler and Pressure Vessel Code (BPVC)*, *Section III: Rules for Constructions of Nuclear Facility Components; Division 1*, American Society of Mechanical Engineers, New York, NY.

Figure 3-11-1—20-in. carbon steel pipeline that failed during hydrotest at gouges on the OD.

Figure 3-11-2—Close-up of Figure 3-11-1 showing the gouges and the fracture origin (arrow) in one of the gouges.

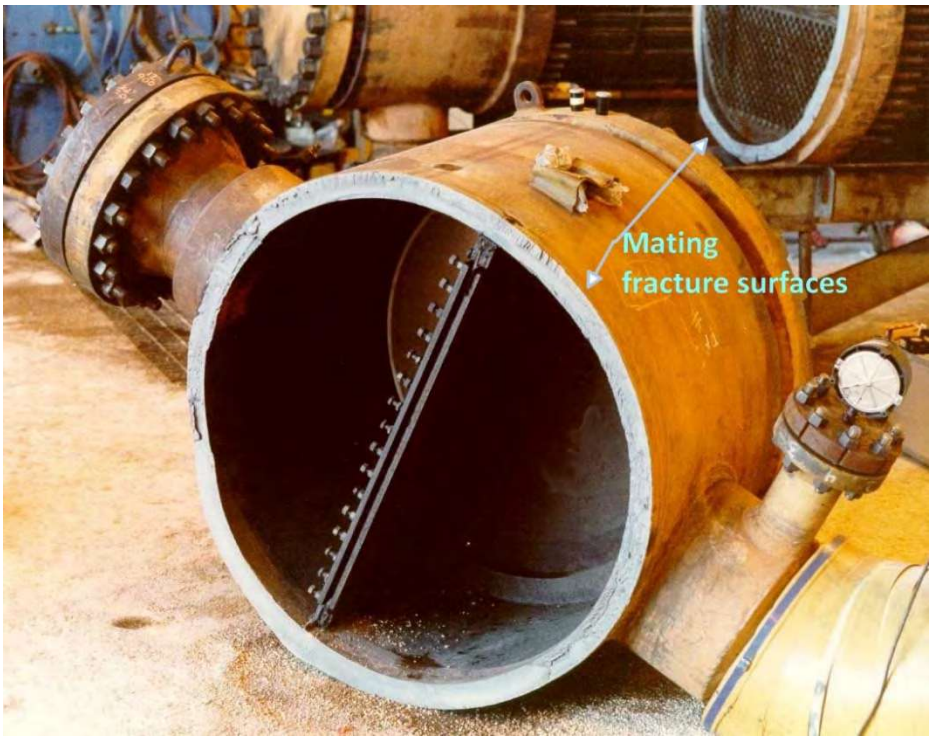


Figure 3-11-3—Brittle fracture of a 2.2-in. wall C-0.5Mo exchanger channel during hydrotest.

Figure 3-11-4—Brittle fracture of vessel shell during hydrotest.

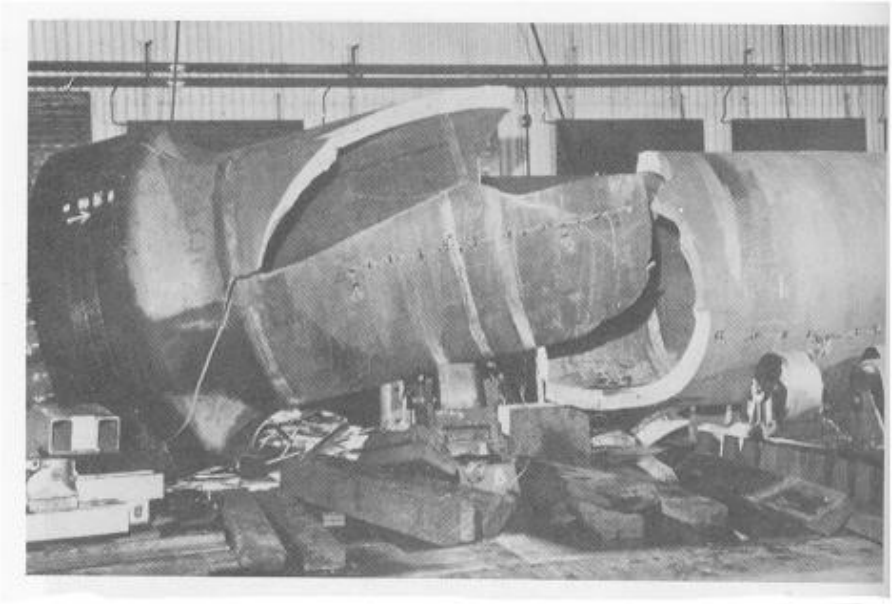


Figure 3-11-5—Classic example of brittle fracture that occurred during hydrotest.

Figure 3-11-6—Close-up view of the fracture surface from a vessel made of A516-70N plate showing the chevron pattern that points back toward the origin of the crack.

3.12 Carbonate Stress Corrosion Cracking

3.12.1 Description of Damage

a) Carbonate SCC, more correctly *alkaline* carbonate SCC (ACSCC), but often referred to as carbonate cracking, occurs in process units containing a free water phase with carbonate ions and where some amount of H_2S is invariably also present.

b) A related type of damage occurs in other environments, causing external cracking of buried pipelines and cracking of piping and equipment handling aqueous carbonate solutions (e.g. potassium carbonate) used for CO_2 removal in hydrogen manufacturing (steam-methane reforming) units. However, these situations are outside the scope of this discussion.

3.12.2 Affected Materials

Carbon steel and low-alloy steels with welds or cold-worked areas.

3.12.3 Critical Factors

a) The weld or cold-worked area must have tensile residual stress and must be in contact with a liquid water phase. The water chemistry is a critical factor affecting the likelihood of carbonate SCC. Cracking is thought to occur when protective surface films (e.g. iron carbonate, iron sulfide, or iron oxides) break down and cannot re-form.

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

c) Crack growth can be sporadic, but rapid, depending on subtle changes in the process.

d) Additional details of water chemistry affecting susceptibility in FCC units are outlined below. More detailed information can be found in Reference 5.

1. pH—The pH of the SW is a critical factor. Based on industry experience, ACSCC does not occur below pH 7. Susceptibility exists in the pH 7.5 to 11 range; however, most failures have occurred in the pH range of 8 to 10. Likelihood increases with increasing pH.

2. H_2S—While cracking occurs alkaline (containing NH_3) water, H_2S is also present in these systems. Destruction of a protective iron sulfide film is thought to be the precursor to carbonate cracking in FCC SWs; however, no threshold level of H_2S affecting carbonate SCC has been established.

3. Ammonia—NH_3 in the SW, which increases the pH, is usually higher in streams where ACSCC has been observed than in cases with no ACSCC. Streams with higher NH_3 and lower H_2S will have a higher pH, which increases the percentage of total carbonate present as carbonate ion and thereby increases the likelihood of ACSCC.

4. Carbonate Ion Concentration—Cracking occurs above a certain threshold concentration of carbonate ions. It has been suggested that levels above 100 ppmw can cause ACSCC, depending on the pH of the system. However, specific thresholds are difficult to define, largely because of the difficulty of sampling and analyzing SW streams for carbonate ions along with the lack of available data.

5. Sulfide-to-Carbonate Ratio—Low ratios of S^{2-} to CO_3^{2-} weaken the protective sulfide scale on steel and increase the likelihood of cracking.

6. Cyanides—Cracking can occur with or without the presence of cyanides.

7. Polysulfides—There is no evidence to suggest that ammonium polysulfide injection increases or decreases the potential for ACSCC.

e) FCC unit feed quality and unit operation appear to have an effect on cracking susceptibility.

1. Feed Nitrogen—The total nitrogen in FCC unit feed is usually higher in cases where ACSCC has been observed than in cases with no ACSCC. Nitrogen compounds tend to increase SW pH.

2. Feed Sulfur—In general, cracking is associated with low-sulfur FCC unit feeds as opposed to high-sulfur feeds. Susceptibility to cracking appears to be much more likely with hydrotreated feed.

3. S-to-N Ratio—Most cases of ACSCC have been associated with a lowering of the S/N ratio in the FCC unit feed to less than 5.

4. Full Burn vs Partial Burn—Full burn increases the regenerator O_2 level, which increases the amount of CO_2 produced and carried back into the reactor. This can directionally increase the tendency for cracking but may be offset by pH depression from increased CO/CO_2 content.

5. Distillate vs Naphtha Optimization—Increasing distillate production from the FCC tends to favor reduced riser temperatures and increased catalyst circulation rates, both of which can increase the flue gas slip back to the reactor and thus the carbonate ion content of the SW streams.

3.12.4 Affected Units or Equipment

a) Carbonate cracking has been most prevalent in FCC unit main fractionator overhead condensing and reflux systems, downstream wet gas compression systems, and the SW systems emanating from these areas. Both piping and vessels are affected. See Figure 3-12-1 and Figure 3-12-2 for typical locations where cracking has occurred.

b) Carbonate SCC has also been observed in the regenerator (cold wall) shell.

c) Carbonate cracking has been observed in pumparound-type SWS units, in the top pumparound and in the ammonia acid gas knockout sections. It has also occurred in highly cold worked pumparound cooler tube u-bends on the OD (process side).

d) Carbonate cracking has also occurred in the floor of a tank storing SW from an FCC unit and in a mercaptan oxidation prewash vessel.

e) Field welds may have higher potential for cracking if high restraint is introduced when making the joint fit-up.

3.12.5 Appearance or Morphology of Damage

a) Carbonate cracks are surface breaking and typically propagate parallel to the weld in the HAZ or adjacent base metal within 2 in. (50 mm) of the weld. At least two cases have occurred more than 3 in. (80 mm) away in highly cold worked fittings including an elbow and reducer.

b) Cracking can also occur in the weld deposit.

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

d) Carbonate cracks are usually found further away from the toe of the weld than cracks resulting from SSC or SOHIC [see (3.67)] and may show up as multiple cracks parallel to a weld. (Figure 3-12-3 and Figure 3-12-4) The appearance of multiple parallel cracks may be related to the low stress required to continue propagating cracks in a loosely adherent scale.

e) Carbonate cracks are predominantly intergranular and typically appear as a network of very fine, oxide-filled cracks similar in appearance to caustic SCC and amine SCC. (See Figure 3-12-5 to Figure 3-12-12.)

3.12.6 Prevention/Mitigation

a) Application of a post-fabrication stress-relieving heat treatment of 1200 °F to 1225 °F (650 °C to 665 °C) in accordance with WRC 452 and WRC 552 (References 8 and 9) is a method of preventing ACSCC. Heat treatment requirements apply to construction and repair welds as well as internal and external attachment welds.

   1. PWHT of highly restrained welds made in the field may still have substantial residual stress remaining after PWHT. (Reference 8)

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

3.12.7 Inspection and Monitoring

a) Monitoring the pH of SWs is the most practical and cost-effective method to locate areas where there is a potential for carbonate cracking to occur. Periodic monitoring of pH and CO_3^{2-} levels should be undertaken to determine the potential for cracking, with concern raised at pH 8 or higher. Sampling and analysis procedures should be verified before their use on highly buffered SW streams.

b) Although cracks may be seen visually, crack detection is best performed with WFMT or ACFM techniques. Surface preparation by grit blasting, high-pressure water blasting, flapper wheel abrasive grinding, or other methods is usually required for WFMT.

c) PT usually cannot find tight or scale-filled cracks and is not recommended.

d) Angle beam UT (SWUT or PAUT) and ECT are effective techniques for crack detection and sizing.

e) Electrical resistance type instruments that measure crack depth are not effective because the cracks typically contain magnetic iron oxide.

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

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

3.12.8 Related Mechanisms

Amine cracking (3.3) and caustic SCC (3.15).

3.12.9 References

1. J.H. Kmetz and D.J. Truax, “Carbonate Stress Corrosion Cracking of Carbon Steel in Refinery FCC Main Fractionator Overhead Systems,” Paper No. 206, *Corrosion/90*, NACE International, Houston, TX.

2. H.U. Schutt, “Intergranular Wet Hydrogen Sulfide Cracking,” Paper No. 454, *Corrosion/92*, NACE International, Houston, TX.

3. E. Mirabel et al., “Carbonate-type Cracking in an FCC Wet Gas Compressor Station,” *Materials Performance*, July 1991, pp. 41–45.

4. NACE Standard RP0296, *Guidelines for Detection, Repair, and Mitigation of Cracking of Existing Petroleum Refinery Pressure Vessels in Wet H_2S Environments*, NACE International, Houston, TX.

5. NACE Publication 34108, *Review and Survey of Alkaline Carbonate Stress Corrosion Cracking in Refinery Sour Waters*, NACE International, Houston, TX, 2008.

6. M. Rivera et al., “Carbonate Cracking Risk Assessment for an FCCU Gas Plant,” Paper No. 04639, *Corrosion/2004*, NACE International, Houston, TX.

7. D. Milton et al., “FCCU Light Ends Plant Carbonate Stress Corrosion Cracking Experience,” Paper No. 07564, *Corrosion/2007*, NACE International, Houston, TX.

8. WRC Bulletin 452*, Recommended Practices for Local Heating of Welds in Pressure Vessels*, Welding Research Council, Shaker Heights, OH, June 2000.

9. WRC Bulletin 552, *Calculation of Weld Residual Stresses and the Effects of Local Post-weld Heat Treatment*, Welding Research Council, Shaker Heights, OH, May 2016.

10. J. Nelson et al., ‘Carbonate Cracking Experiences in Unusual Locations,” Paper No. 9596, *Corrosion/2017*, NACE International, Houston, TX.

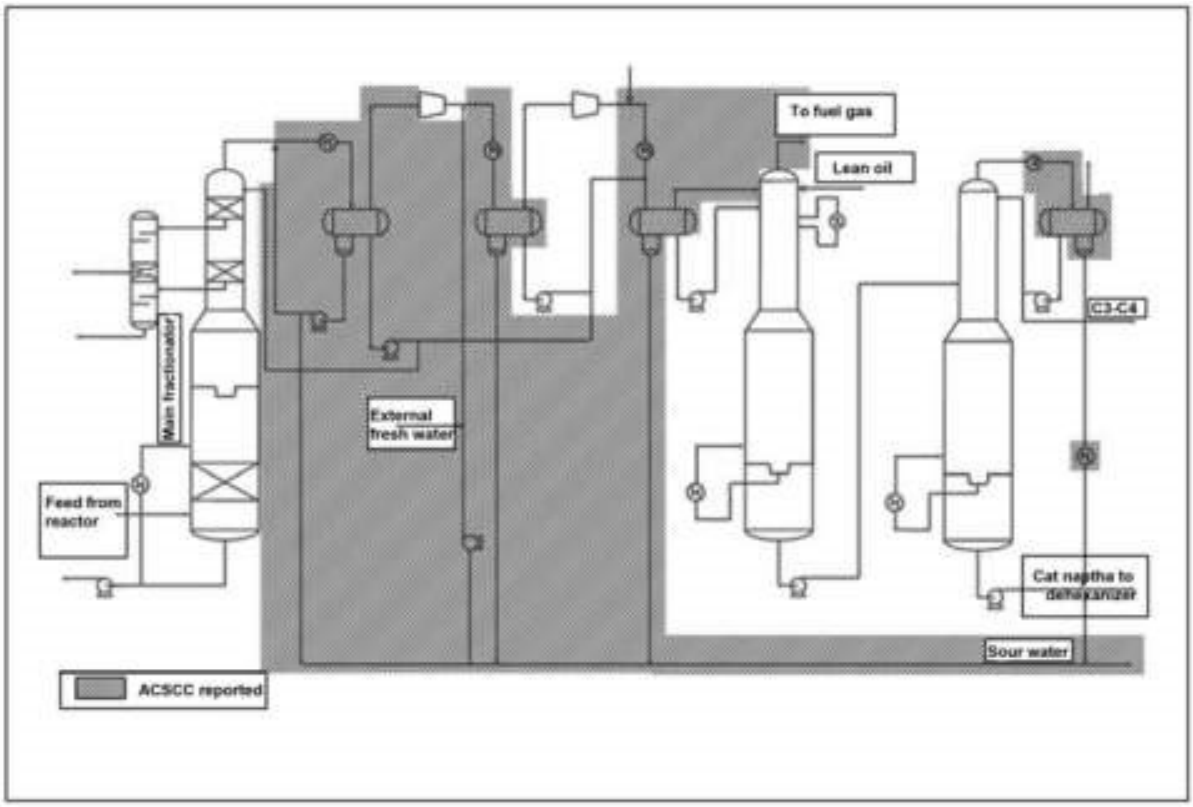


Figure 3-12-1—Simplified PFD of an FCC unit gas plant showing where ACSCC has been reported. (Reference 5)

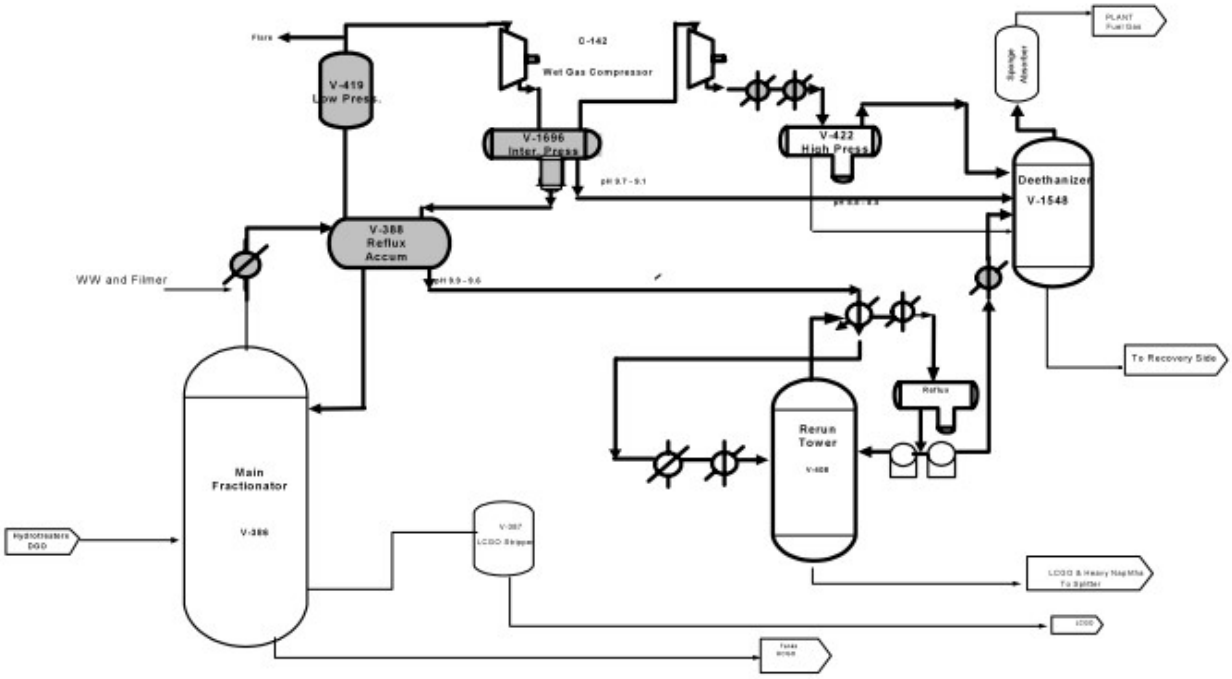


Figure 3-12-2—In a span of 7 months, a refinery experienced 23 leaks in piping in the fractionator overhead and the wet gas compressor sections. Follow-up with SWUT located 73 more indications. (Reference 6)

Figure 3-12-3—Carbonate cracking in an overhead interstage knockout drum vapor outlet nozzle.

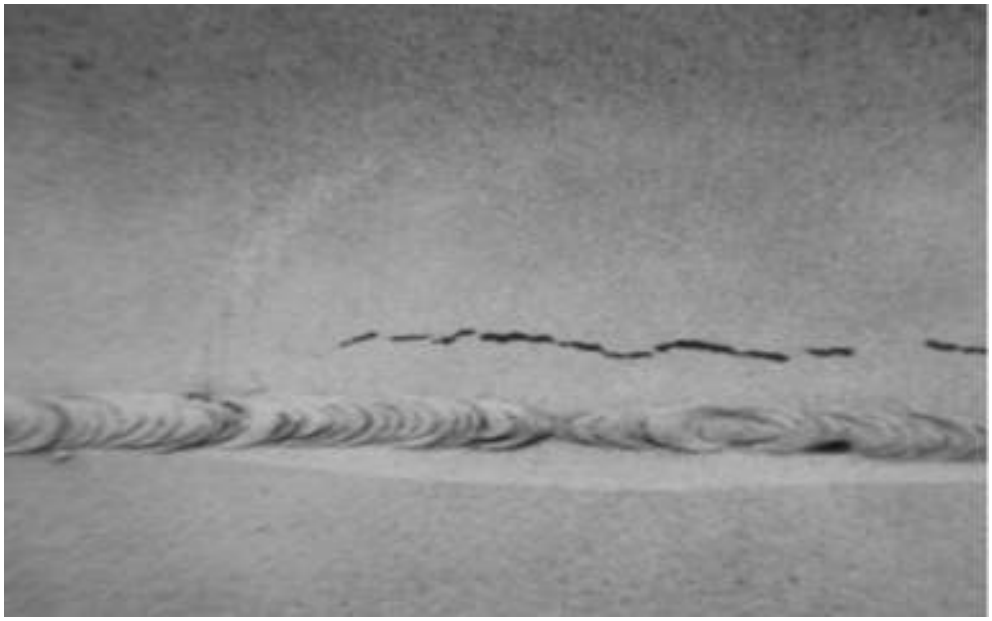


Figure 3-12-4—Carbonate cracking adjacent to a weld. (Reference 6)

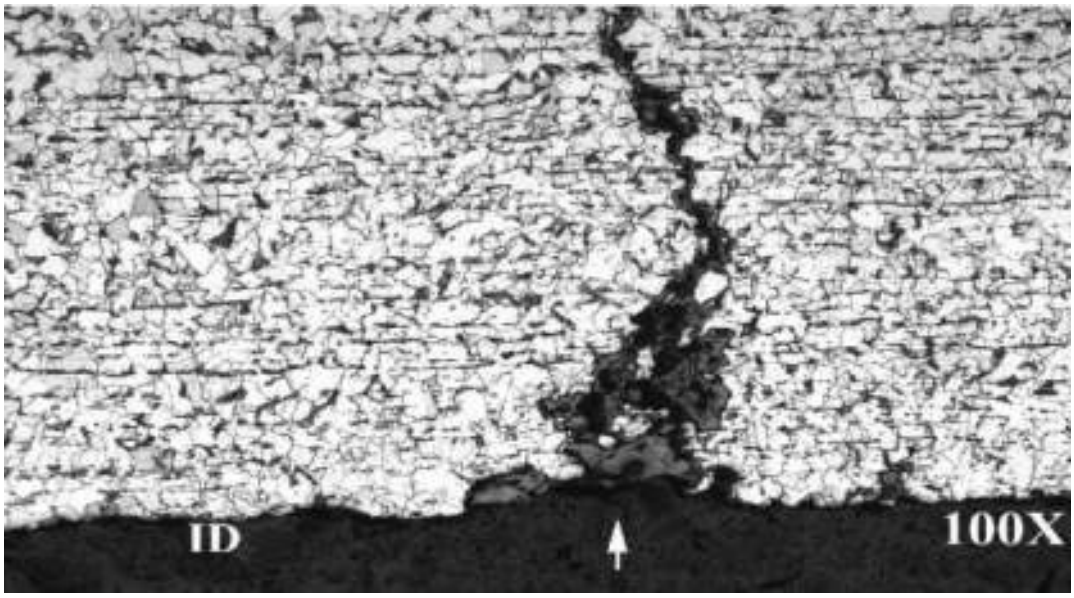


Figure 3-12-5—Metallographic sample showing intergranular carbonate cracking that developed after 6 months of service. (Reference 6)

Figure 3-12-6—Most cracks originate in base metal, but this weldment contained a crack that originated at the root and propagated through the weld metal. Other cracks appear to have initiated in the HAZ. (Reference 7)

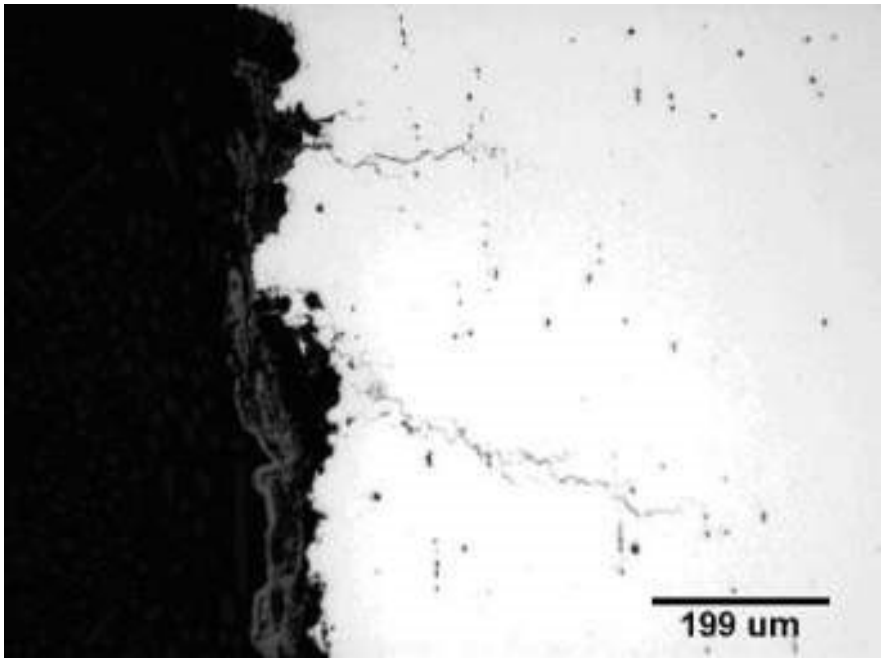


Figure 3-12-7—Photomicrograph of carbonate cracking in the base metal. Cracks initiated from the ID surface (left side). Unetched.

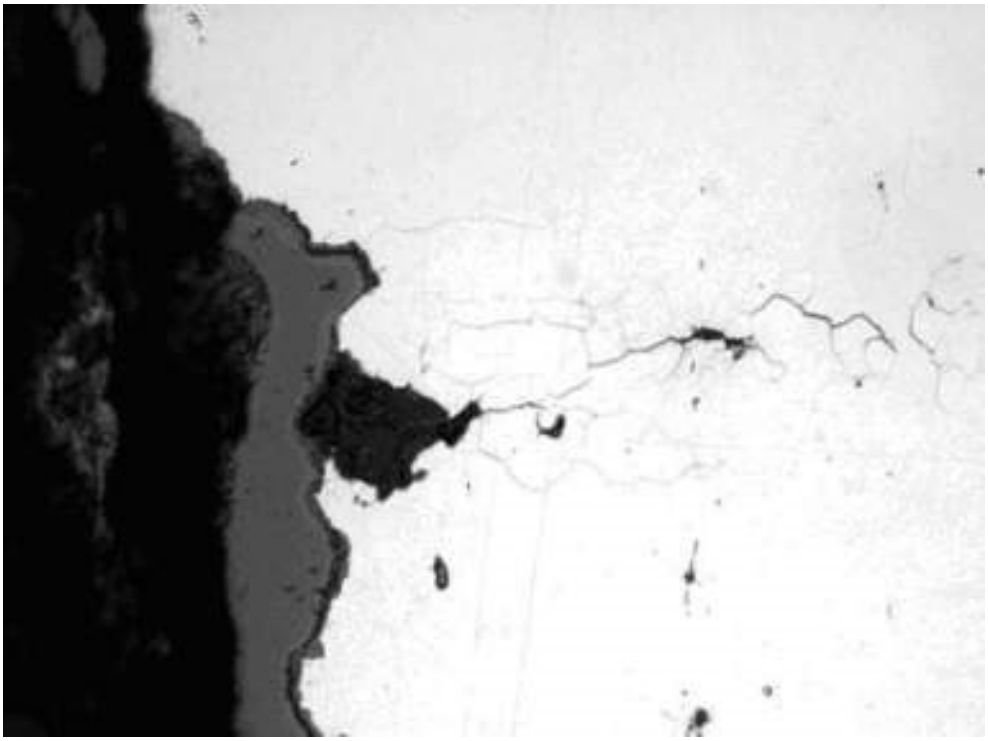


Figure 3-12-8—Photomicrograph of carbonate cracking in the base metal, initiating at a corrosion pit on the ID surface. Unetched.

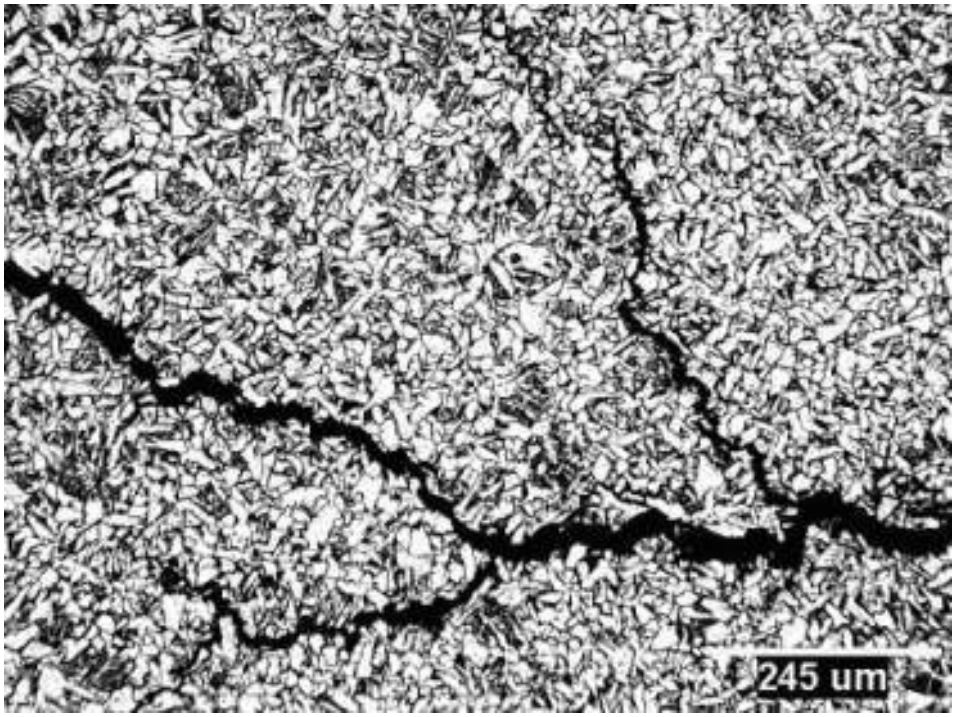


Figure 3-12-9—Photomicrograph of carbonate cracking in the base metal, showing the branched nature of the cracking. Etched.

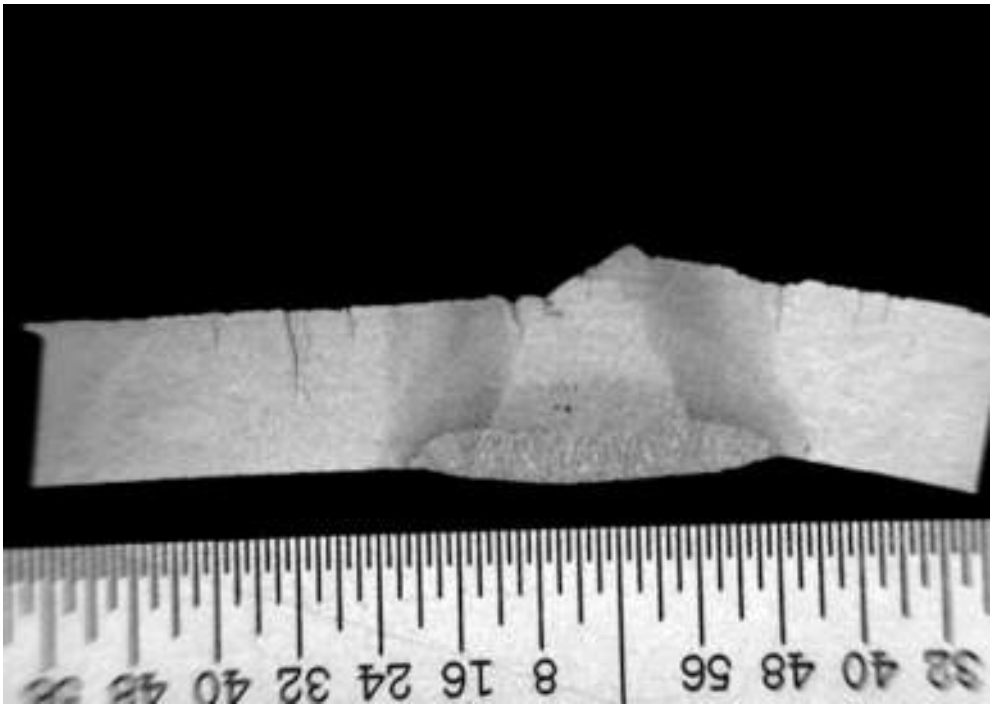


Figure 3-12-10—A weld from a 4-in. (100 mm) ASTM A53 reflux line on the main fractionator that leaked after 52 years of service.

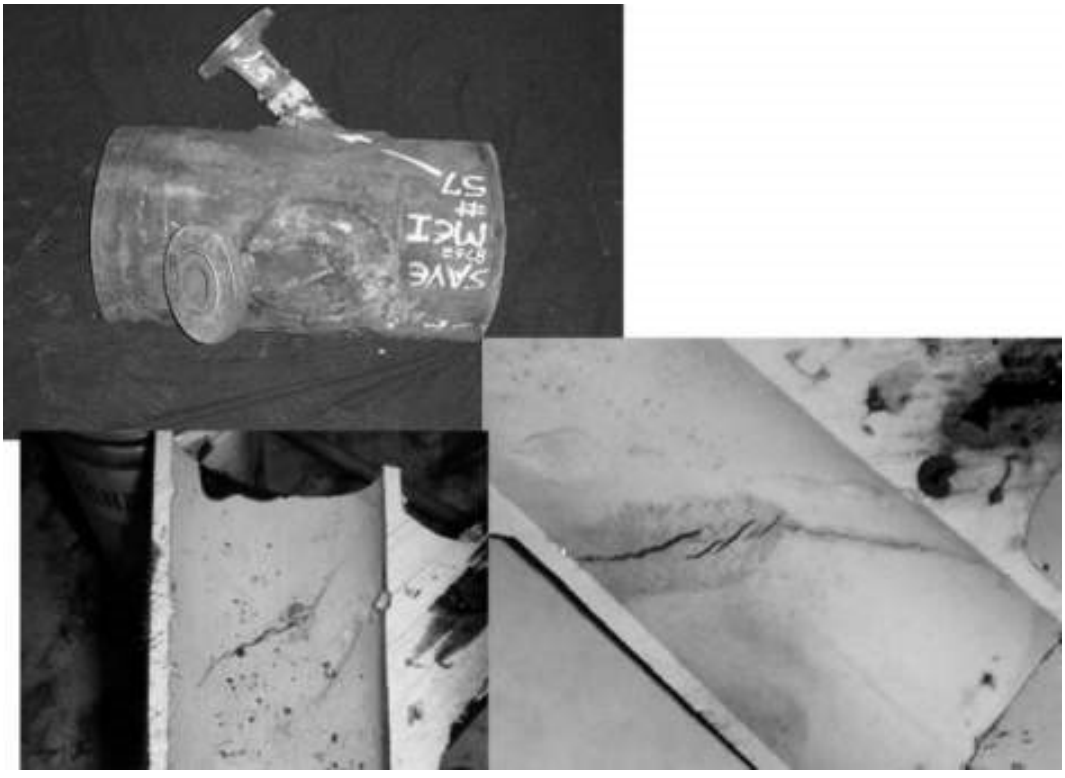


Figure 3-12-11—An 18-in. (460-mm) diameter API 5L Grade B pipe section with two 1-in. (25-mm) water wash injection nozzles from the inlet to the 2nd stage compressor. Note the cracks on the IDs of the two injection nozzles after blast cleaning. The line leaked after 21 years of service.

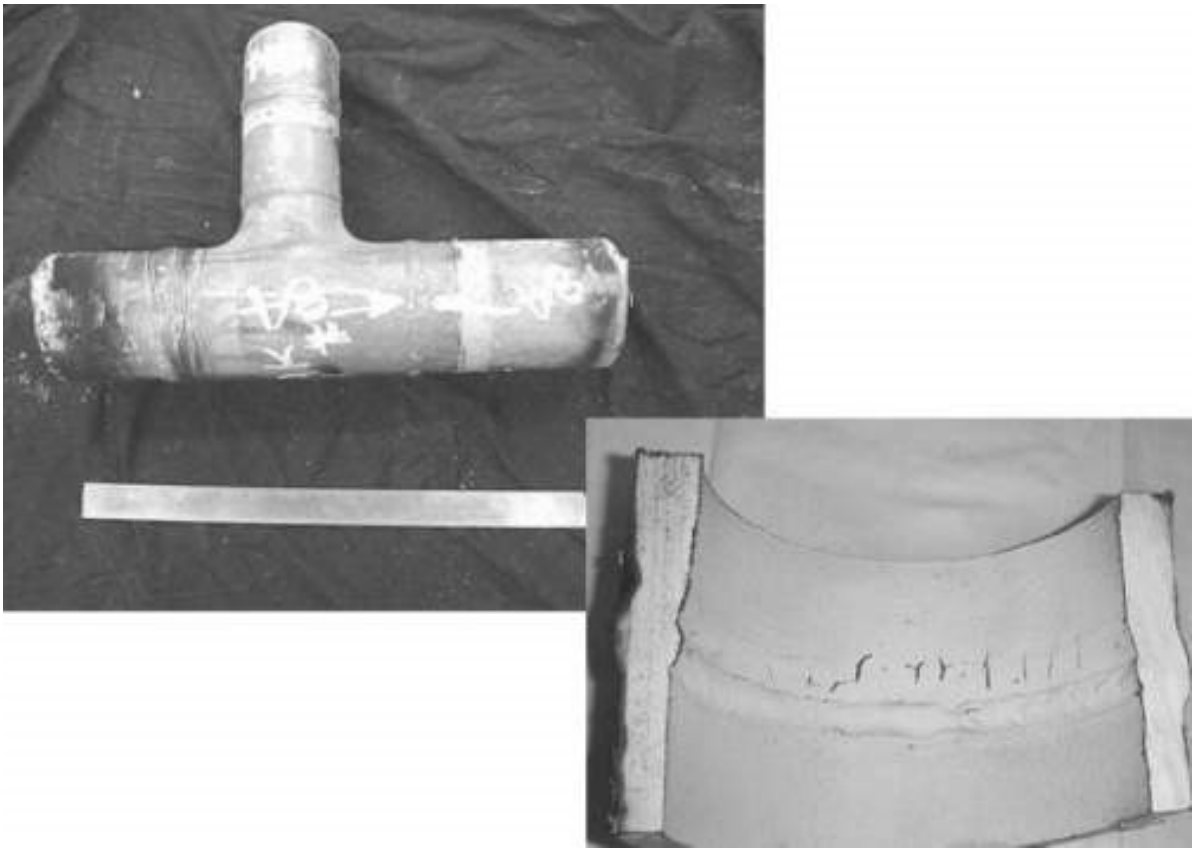


Figure 3-12-12—A 3-in. x 4-in. (75-mm x 100-mm) diameter tee in a hydrocarbon line off a water knockout pot in the FCC light ends recovery section. Cracking developed after 6 months of service.

3.13 Carburization

3.13.1 Description of Damage

Carbon is absorbed into a material at elevated temperature while in contact with a carbonaceous material or carburizing environment. Carburized steel is brittle and may spall or crack. Carburization can reduce (or eliminate) the remaining sound metal wall thickness and may also reduce the corrosion resistance of stainless steel.

3.13.2 Affected Materials

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

3.13.3 Critical Factors

a) Three conditions must be satisfied:

1. exposure to a carburizing environment or carbonaceous material;
2. temperature high enough to allow diffusion of carbon into the metal [typically above 1100 °F (595 °C)];
3. susceptible material.

b) Conditions favoring carburization include a high gas phase carbon activity (hydrocarbons, coke, gases rich in CO, CO_2, CH_4, ethane) and low oxygen potential (minimal O_2 or steam).

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

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

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

f) Carburization of 300 series SS can result in a reduction of chromium levels available to provide corrosion protection. This has caused accelerated sulfidation of 300 series SS in coker furnaces.

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

3.13.4 Affected Units or Equipment

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

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

c) Carburization is sometimes found in heater tubes in catalytic reformers and coker units or other heaters where coke can form.

d) Carburization is also encountered in ethylene pyrolysis and steam reformer furnaces.

3.13.5 Appearance or Morphology of Damage

a) The depth of carburization can be confirmed by metallography. (Figure 3-13-1 and Figure 3-13-2)

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

c) In a more advanced stage, there may be a volumetric increase in the affected component. In this situation, carbides that form can cause the surrounding metal to “crumble” due to the increase in volume. This has been termed “catastrophic carburization” and has resulted in significant metal loss over an extended period of time.

d) Severe cases may also result in bulges, heavy scale, thin-line brittle cracking, and/or “thick-lip” tube failures. Cracking can also have a “crow’s feet” appearance.

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

f) Carburization results in the formation of metal carbides depleting the surrounding matrix of the carbide-forming element.

3.13.6 Prevention/Mitigation

a) Select alloys with adequate resistance to carburization. This typically includes alloys that form stable oxides on the surface. This benefit is commonly achieved using an alumina-forming coating commonly referred to as alonizing.

b) Reduce the carbon activity of the process environment.

c) Add low levels of a reactive sulfur compound to the process stream to prevent the absorption of carbon on the surface of the metal. Typically, sulfur levels less than 10 ppm are needed to prevent carburization.

3.13.7 Inspection and Monitoring

a) VT is ineffective in detecting carburization. A-scan UT is ineffective at determining carburized thickness.

b) Carburization can be determined accurately by destructive sampling, i.e. sampling for chemical and/or physical testing.

c) Inspection for carburization in the initial stages of attack is difficult. If the process-side surfaces are accessible, hardness testing and field metallography (replication) can be used. Destructive sampling and electromagnetic based techniques (eddy current) have also been used.

    1. In situ metallography (replication) is rarely used alone for evaluation of carburization and is best used in combination with other NDE techniques.

    2. Hardness testing carries the same caution as hammer testing for heavily carburized tubes, as it may create a brittle fracture initiation site.

d) Carburization causes the normally nonmagnetic wrought and cast heat-resistant alloys to become magnetic. The resulting magnetic permeability provides a methodology for monitoring the extent of carburization damage. Inspection techniques based on determining increased levels of ferromagnetism (magnetic permeability) are also useful for alloys that are paramagnetic when initially installed (austenitic alloys).

e) Measurement devices range from simple hand-held magnets to advanced multi-frequency eddy current instruments. However, surface oxides may interfere with the results.

f) Some instruments and field services can relate the degree of magnetism to the depth of carburization. Most of the instruments are proprietary, and the field services are limited.

g) In the advanced stages of carburization where cracking has initiated, RT, UT, and some magnetic techniques, which can be combined for effectiveness, may be used.

h) Specialized time of flight diffraction (TOFD) has been used to determine the case depth of carburization but requires trained technicians for application and interpretation.

i) Cast austenitic stainless steel tubes and Cr-Mo ferritic alloy tubes in fired heater/boiler service should not be hammer tested when tubes are heavily carburized.

3.13.8 Related Mechanisms

Metal dusting (3.44).

3.13.9 References

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

2. H.J. Grabke, *Carburization: A High Temperature Corrosion Phenomenon*, Part 1: State-of-the-Art Review; Part 2: Best Practices for Testing Alloys, MTI Publication No. 52.

3. API Recommended Practice 939-C, *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries*, American Petroleum Institute, Washington, DC

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

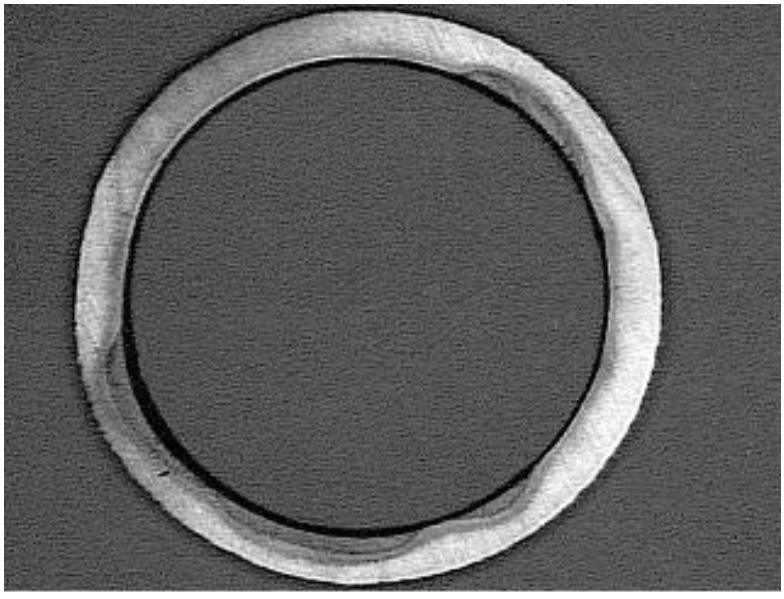


Figure 3-13-1—Carburization (dark areas) of an HP-modified tube from an ethylene furnace after 3 years at 1900 °F (1040 °C).

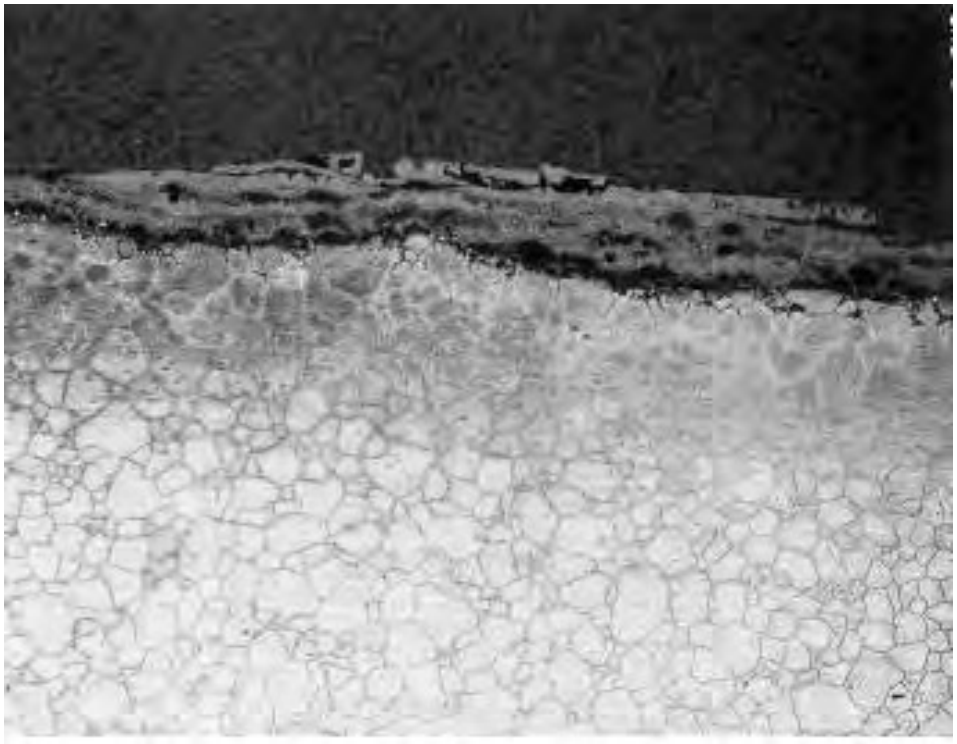


Figure 3-13-2—A photomicrograph of a cross section of a 304H cyclone from a fluid coker showing surface carburization after 24 years. Magnification 35X.

3.14 Caustic Corrosion

3.14.1 Description of Damage

Localized corrosion due to the concentration of caustic (alkaline) solutions such as NaOH and KOH, and/or corrosive salts from those solutions, that usually occurs under evaporative or high heat transfer conditions (commonly called caustic gouging). Also, corrosion resulting in general thinning can occur at elevated temperatures, depending on alkali or caustic solution strength.

3.14.2 Affected Materials

Primarily carbon steel, low-alloy steels, and 400 series SS. Carbon steel is the material most commonly used in situations where caustic corrosion is a concern. 300 series SS is generally resistant to caustic corrosion until passivity is damaged, which can occur in the approximate temperature range of 160 °F to 210 °F (70 °C to 100 °C), depending on the concentration. 300 series SS can also be susceptible to caustic SCC at these elevated temperatures. (See 3.15.)

3.14.3 Critical Factors

a) Caustic (NaOH or KOH) must be present. The following are sources of caustic.

   1. Caustic is commonly added to treat BFW and may also enter inadvertently during regeneration of demineralizers.

   2. Caustic is sometimes added to process streams for acid neutralization or as a reactant to remove sulfur or chlorides.

   3. Alkaline solutions or salts may also enter process streams through leaks in condensers or other process equipment.

   4. Concentrated caustic is handled in the storage and feed equipment used for feeding caustic into BFW or process streams.

b) In high-solution-strength caustic, temperatures above about 170 °F (75 °C), with the temperature limit depending on the caustic concentration, will cause general corrosion of carbon steel. (See Figure 3-15-1 in 3.15 on caustic SCC.)

c) For localized caustic gouging to occur, a concentrating mechanism must exist to build up the caustic strength or salt concentration.

   1. Caustic can become concentrated by departure from nucleate boiling (DNB), evaporation, and deposition of salts.

   2. Higher temperatures help produce a concentrating mechanism, thereby increasing the corrosivity of the solution while also generally increasing the corrosion rate.

d) Some contaminants, such as chlorides and hypochlorites, are known to increase the corrosivity of caustic solutions.

e) Heat tracing may sometimes contribute to this problem.

3.14.4 Affected Units or Equipment

a) Localized caustic corrosion (caustic gouging) is most often associated with boilers and steam-generating equipment including heat exchangers. This also applies to steam-generating equipment in H_2 manufacturing units and steam generators within other process units.

b) Similar concentrating effects of caustic can occur where caustic is added to crude unit feed.

1. Accelerated localized corrosion can occur in preheat exchangers, furnace tubes, and transfer lines, if the caustic is not effectively mixed in the oil stream.

c) Units that use caustic for removing sulfur compounds from process streams can also be subject to caustic corrosion.

d) Heat-traced tanks used for caustic storage and caustic feed equipment near the process injection location can suffer caustic corrosion if temperatures get too high.

3.14.5 Appearance or Morphology of Damage

a) Caustic gouging is typically characterized by localized metal loss that may appear as grooves in a boiler tube or locally thinned areas under insulating deposits. (Figure 3-14-1 and Figure 3-14-2)

b) Deposits may fill corroded depressions and mask damage below. Probing suspect areas with a sharp instrument may be required.

c) Localized gouging may result along a waterline where corrosives concentrate. In vertical tubes, this may appear as a circumferential groove.

d) In horizontal or sloped tubes, grooving may appear at the top of the tube or as longitudinal grooves on opposite sides of the tube.

e) Corrosion of carbon steel in high-concentration caustic at elevated temperatures will be generalized but likely confined to the location of the high temperature, e.g. next to heat tracing.

3.14.6 Prevention/Mitigation

a) In steam-generating equipment, caustic corrosion is best prevented through proper design. Damage can be minimized by reducing the amount of free caustic, by ensuring adequate water flooding and water flow, by ensuring proper burner management to minimize hot spots on heater tubes, and by minimizing the ingress of alkaline producing salts into condensers.

b) In process equipment, caustic injection facilities should be designed to allow proper mixing and adequate dilution of caustic in order to avoid the concentration of caustic on hot metal surfaces.

c) Carbon steel (and stainless steels) have serious corrosion problems in high-strength caustic solutions at elevated temperatures. Alloy 400 and some other nickel-based alloys exhibit much lower corrosion rates.

3.14.7 Inspection and Monitoring

a) General Corrosion—UT using a straight beam or UT scanning or other similar techniques can measure general loss.

b) Localized Corrosion—Manual UT, including UT scanning, or AUT can be used. Angle beam (SWUT or PAUT) or TOFD may be necessary to determine the extent of localized corrosion. RT has also been used within the limits of the technique.

c) Permanently mounted thickness monitoring sensors can be used.

d) Heat or steam tracing can cause localized corrosion at the point of contact due to locally high temperatures or improper installation. This is an area to focus on for inspection.

e) Caustic injection sites should be examined and monitored as discussed in API 570 and API 574.

f) When internal access is not available (e.g. steam equipment, tubing, small-diameter equipment, or equipment with ports), VT may be performed using a boroscope.

3.14.8 Related Mechanisms

Caustic SCC (3.15). Caustic gouging has also been referred to as ductile gouging.

3.14.9 References

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

2. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991, pp. 58–70.

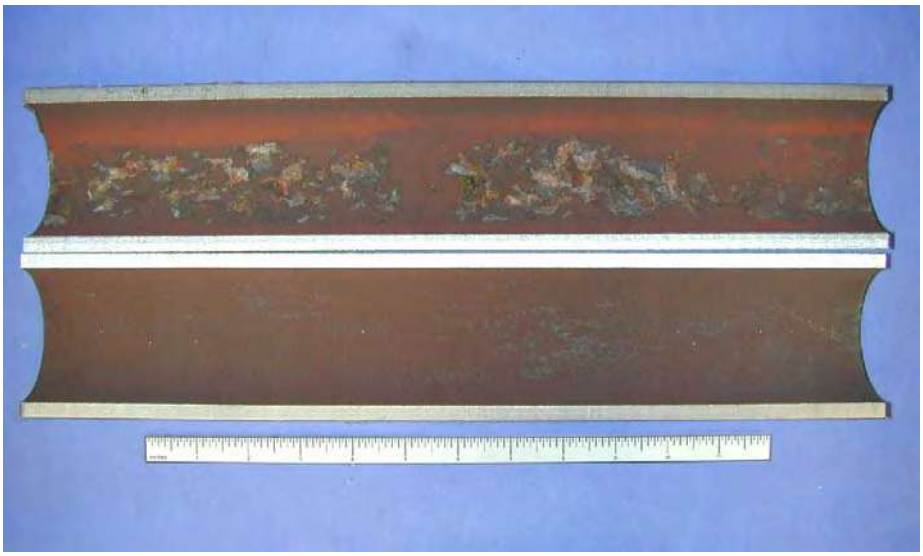


Figure 3-14-1—ID deposits on carbon steel boiler tube with damage due to caustic corrosion.

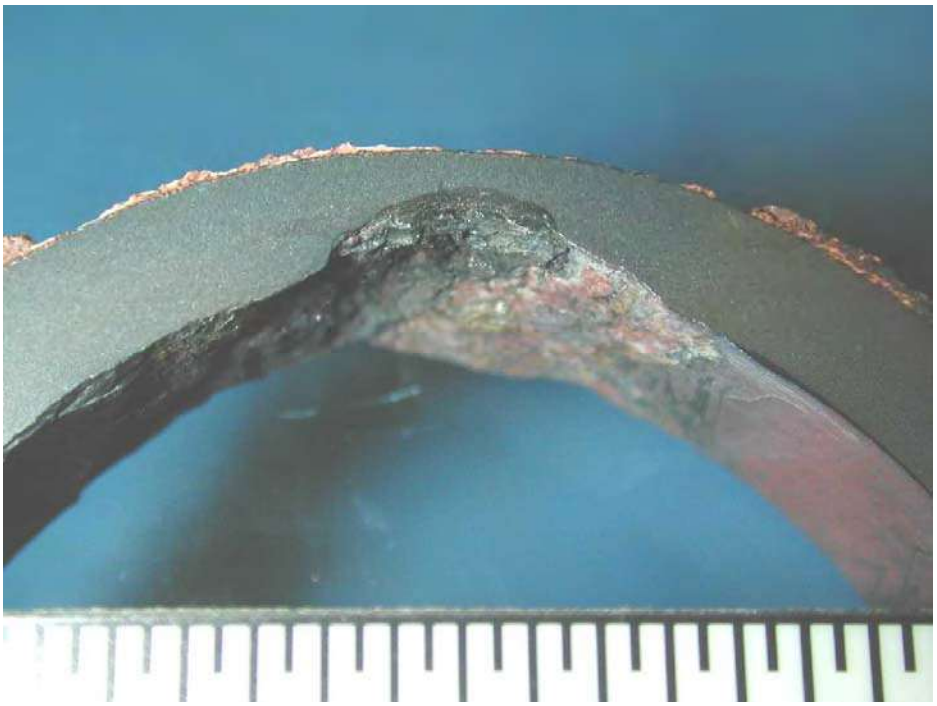


Figure 3-14-2—Cross section of tube in Figure 3-14-1 showing localized attack due to caustic corrosion.

3.15 Caustic Stress Corrosion Cracking

3.15.1 Description of Damage

Caustic SCC is characterized by surface-initiated cracks that occur in piping and equipment exposed to caustic (alkaline hydroxide solutions) at elevated temperature, primarily adjacent to non-PWHT'd welds. It is a form of ASCC. The temperature above which caustic SCC occurs depends on the concentration of the caustic solution.

3.15.2 Affected Materials

Carbon steel, low-alloy steels, and 300 series SS are susceptible. Duplex stainless steels are also susceptible but have shown improved resistance compared to the 300 series SS. Nickel-based alloys are more resistant.

3.15.3 Critical Factors

a) Susceptibility to caustic SCC in caustic soda (NaOH) and caustic potash (KOH) solutions is a function of caustic strength, metal temperature, and stress level.

b) Increasing caustic concentration and increasing temperature increase the likelihood and rate of cracking. Conditions likely to result in cracking have been established through plant experience and are presented in Figure 3-15-1.

c) Cracking can occur at low caustic levels if a concentrating mechanism is present. In such cases, caustic concentrations of 50 ppm to 100 ppm are sufficient to cause cracking.

d) Residual stresses from welding (in non-stress-relieved welds) or from cold working (such as bending and forming) will cause cracking, and these high residual stresses are what typically lead to caustic SCC. (Figure 3-15-2 to Figure 3-15-8) Applied stresses, e.g. from pressure or mechanical loading, can also cause caustic SCC, but this is uncommon since applied stresses are normally low relative to the yield point and are lower than residual stresses from welding or forming.

e) Thermal stress relief (PWHT) is effective in preventing caustic SCC. (Figure 3-15-1)

f) Crack propagation rates increase dramatically with temperature, and cracks can grow through wall in a matter of hours during temperature excursions, especially in concentrated caustic or if conditions promote caustic concentration. Concentration can occur as the result of alternating wet and dry conditions, localized hot spots, or high-temperature steam out.

g) Special care must be taken with steam tracing or heat tracing design as well as steam out of non-PWHT'd piping and equipment.

h) Contaminants in the caustic solution, especially sulfides, regardless of concentration, will increase the likelihood of SCC in non-PWHT'd carbon steel, including in the lower temperature area (area "A") in Figure 3-15-1.

3.15.4 Affected Units or Equipment

a) Caustic SCC can occur in non-stress-relieved piping and equipment that handles caustic, including H_2S and mercaptan removal units, as well as equipment that uses caustic for neutralization in sulfuric acid alkylation units and HF alkylation units. Caustic is sometimes injected into the feed to the crude tower for chloride control.

b) Failures have occurred in improperly heat-traced piping or equipment as well as heating coils and other heat transfer equipment.

c) Caustic SCC can occur in equipment as the result of steam cleaning after being in caustic service.

d) Traces of caustic can become concentrated in BFW and can result in caustic SCC of boiler tubes that alternate between wet and dry conditions due to overfiring. It can also occur in superheaters due to steam drum carryover.

e) Cracking can occur in boilers at rolled tube joints due to caustic concentrating between the tube and tubesheet. (Figure 3-15-4)

f) Caustic SCC can also occur as the result of unintended carryover of caustic into equipment not designed to handle hot caustic (e.g. not stress relieved), such as steam condensate piping or process equipment downstream of a caustic treating section of a process unit.

3.15.5 Appearance or Morphology of Damage

a) Caustic SCC typically propagates parallel to the weld in adjacent base metal, i.e. in the zone of highest welding residual stress, but can also occur in the weld deposit or HAZ and can be transverse to the weld.

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

c) Cracks can be confirmed through metallographic examination. Cracks are typically branched and predominantly intergranular. Cracking that occurs in as-welded carbon steel typically appears as a network of very fine, oxide-filled cracks.

d) Cracking in 300 series SS is most often transgranular but can be intergranular even in non-sensitized material. When transgranular, it can be difficult to distinguish from Cl^- SCC. Caustic SCC should exhibit a black magnetite layer on the crack surface, whereas Cl^- SCC should not produce that type of oxide scale.

e) Similarly, caustic SCC of nickel-based alloys has been observed as either intergranular (Figure 3-15-9) or transgranular (Figure 3-15-10).

3.15.6 Prevention/Mitigation

a) Cracking can be effectively prevented by means of a stress-relieving heat treatment (e.g. PWHT). A heat treatment at 1150 °F (620 °C) minimum with a minimum holding time of 1 hr is considered an effective stress relieving heat treatment for carbon steel. The same requirement applies to repair welds and to internal and external attachment welds.

   1. In contaminated caustic solutions, stress relief may be needed to prevent cracking of carbon steel even at low, otherwise “safe” temperatures (area “A” in Figure 3-15-1).

b) 300 series SS offer little advantage in resistance to cracking over carbon steel.

c) Nickel-based alloys are more resistant to cracking and may be required at higher temperatures and/or caustic concentrations. However, caustic SCC of these alloys has been observed at high temperatures that promote the formation of molten caustic in the absence of free water [604 °F (318 °C), at atmospheric pressure]. This damage has sometimes been referred to as molten caustic cracking.

d) Steam out of non-PWHT’d carbon steel piping and equipment should be avoided. Where necessary, equipment should be water washed before steaming out, and only low-pressure steam should be used for short periods of time to minimize exposure.

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

f) Ensure all soda ash (sodium carbonate) solution that may have been used as a protective measure against polythionic acid stress corrosion cracking (PTA SCC) in 300 series SS equipment is drained prior to heating up as this soda ash can result in caustic SCC of 300 series SS as well as Alloy 800 and Alloy 825 as the water is boiled away.

3.15.7 Inspection and Monitoring

a) WFMT, ACFM, and ECT can be effective techniques to detect these surface-breaking cracks. Proper surface preparation is necessary to ensure cracking is not masked by blending or smearing metal into the cracks. The method of surface preparation is dependent upon the specific technique.

b) Angle beam ultrasonic techniques (SWUT and PAUT) can be effective to detect and size cracks. These ultrasonic techniques can be used to periodically monitor crack growth.

c) PT or MT can be effective. PT may not be effective for finding tight cracks, because the cracks are oxide filled.

d) RT may not be effective in detecting fine, tight cracks.

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

f) Severe cracking can at times be identified visually.

3.15.8 Related Mechanisms

Amine SCC (3.3) and carbonate SCC (3.12) are two other similar forms of ASCC. Caustic SCC has also been called caustic embrittlement, but this is a misnomer and an obsolete term. Caustic SCC is a SCC mechanism, not an embrittlement mechanism.

3.15.9 References

1. NACE 37519, *NACE Corrosion Data Survey—Metals Section*, Fifth Edition, NACE International, Houston, TX.

2. “Fitness-For-Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service,” Materials Properties Council, FS-26, Draft No. 5, Consultants Report, NY, 1995.

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

4. NACE SP0403, *Avoiding Caustic Stress Corrosion Cracking of Refinery Equipment and Piping*, NACE International, Houston, TX.

5. REFIN•COR, Corrosion Technology Week, 2011, NACE International, Houston, TX.

6. “Environmentally Assisted Cracking,” *ASM Handbook—Corrosion: Environments and Industries*, Volume 13C, ASM International, Materials Park, OH, 2007.

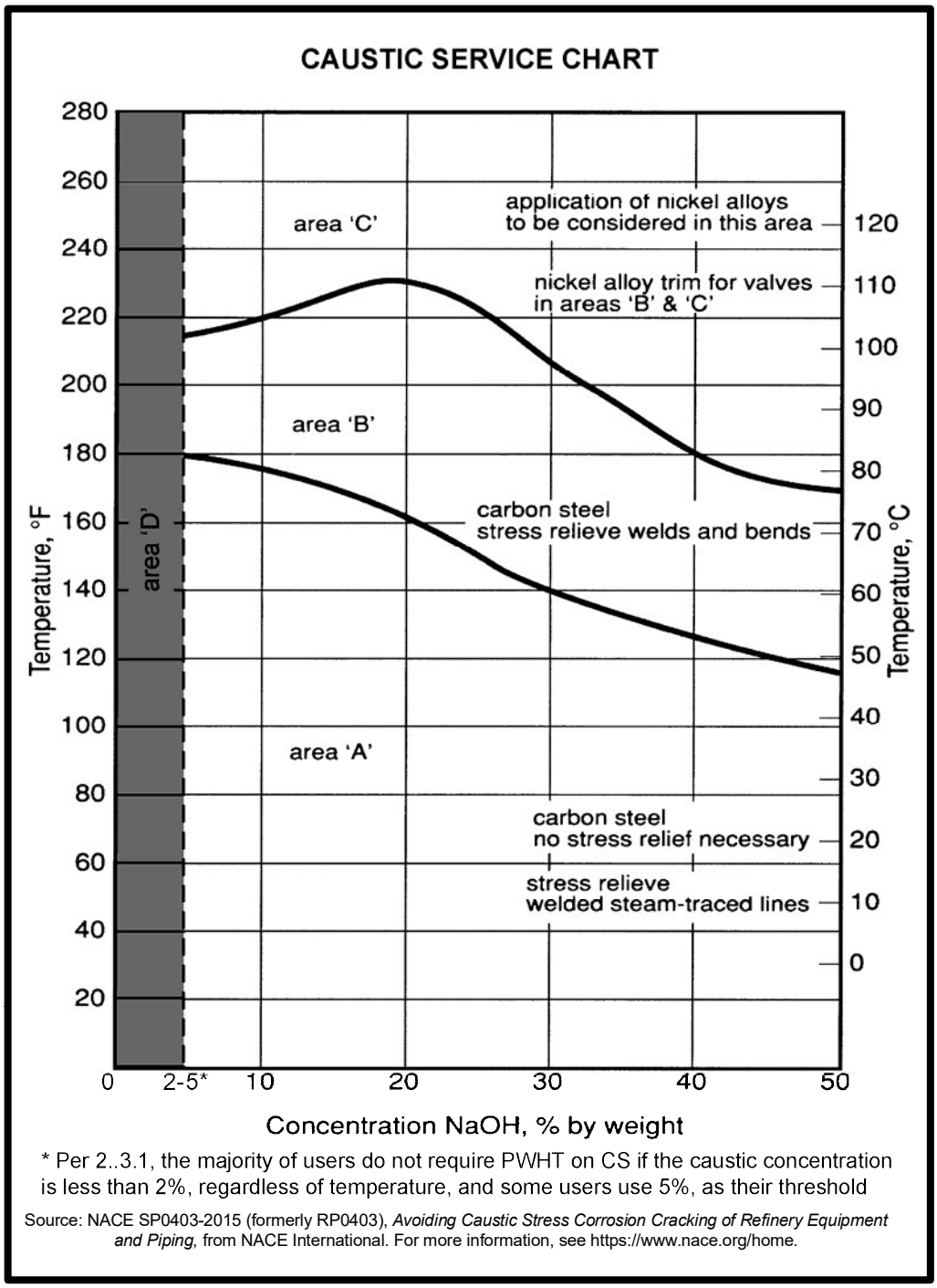


Figure 3-15-1—Recommended operating limits for carbon steel in caustic service. (Reference 4)

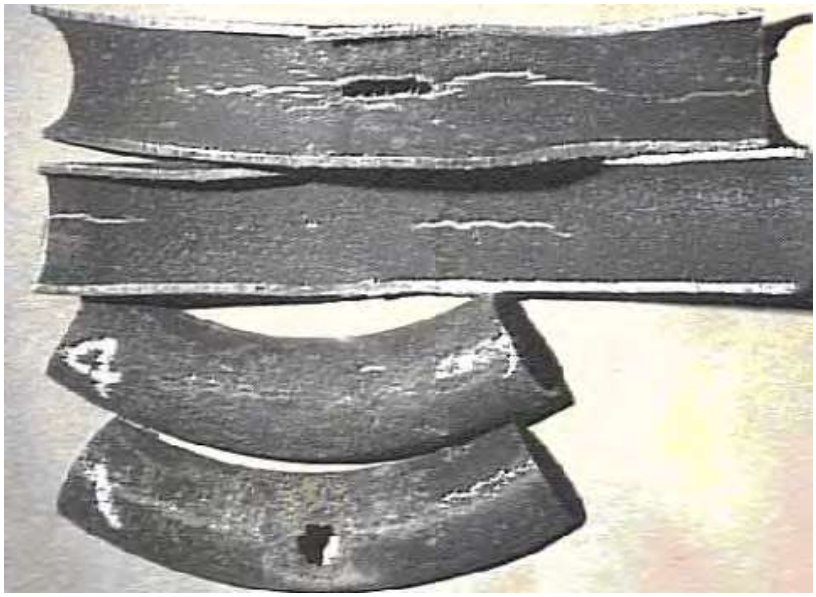


Figure 3-15-2—Cracking initiating on the inside surface of a non-stress-relieved carbon steel heat exchanger bend after 8 years in 15 % to 20 % caustic service at 140 °F to 240 °F (60 °C to 115 °C).

Figure 3-15-3—Photomicrograph of a crack in the tube shown in Figure 3-15-2.

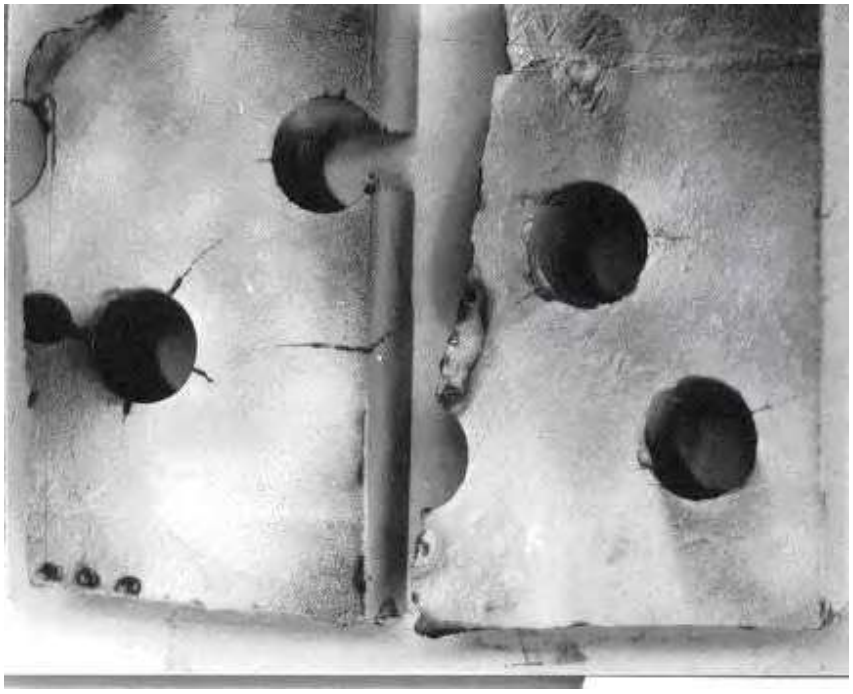


Figure 3-15-4—Cracking in a boiler tubesheet due to caustic concentrating between the tube and the tubesheet.

Figure 3-15-5—Photomicrograph of a crack in the tubesheet shown in Figure 3-15-4.

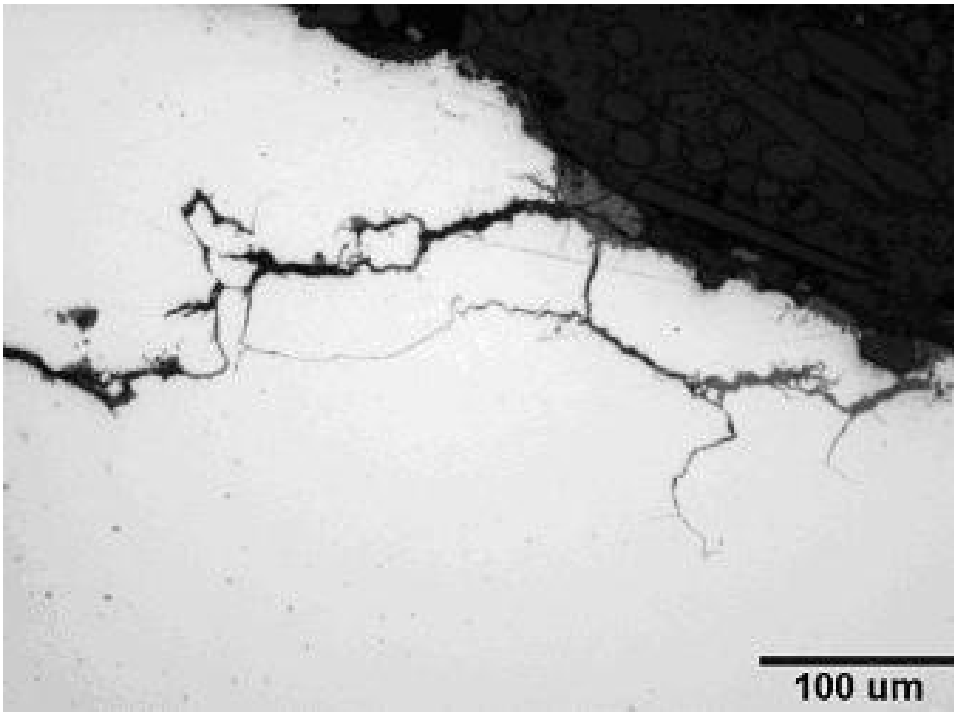


Figure 3-15-6—Photomicrograph of caustic cracking initiating on the ID of a carbon steel socket weld in non-PWHT'd piping in a suction drum downstream of a caustic scrubber. Unetched.

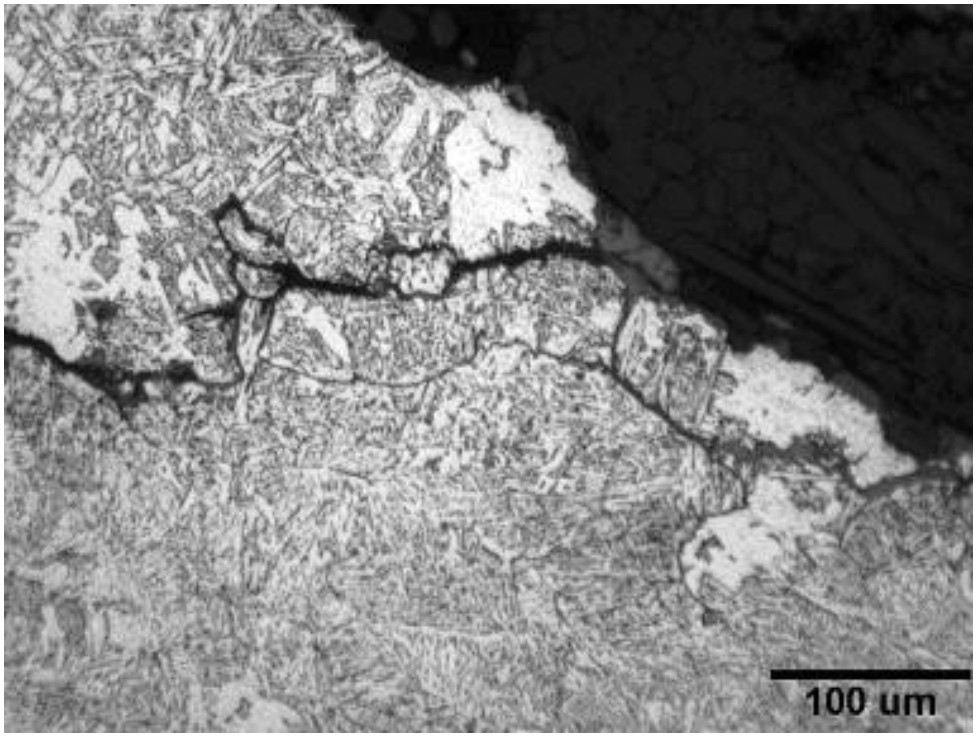


Figure 3-15-7—Figure 3-15-6 in the etched condition.

Figure 3-15-8—Stainless steel expansion bellows from a steam-driven turbine previously subjected to a caustic carryover upset condition.

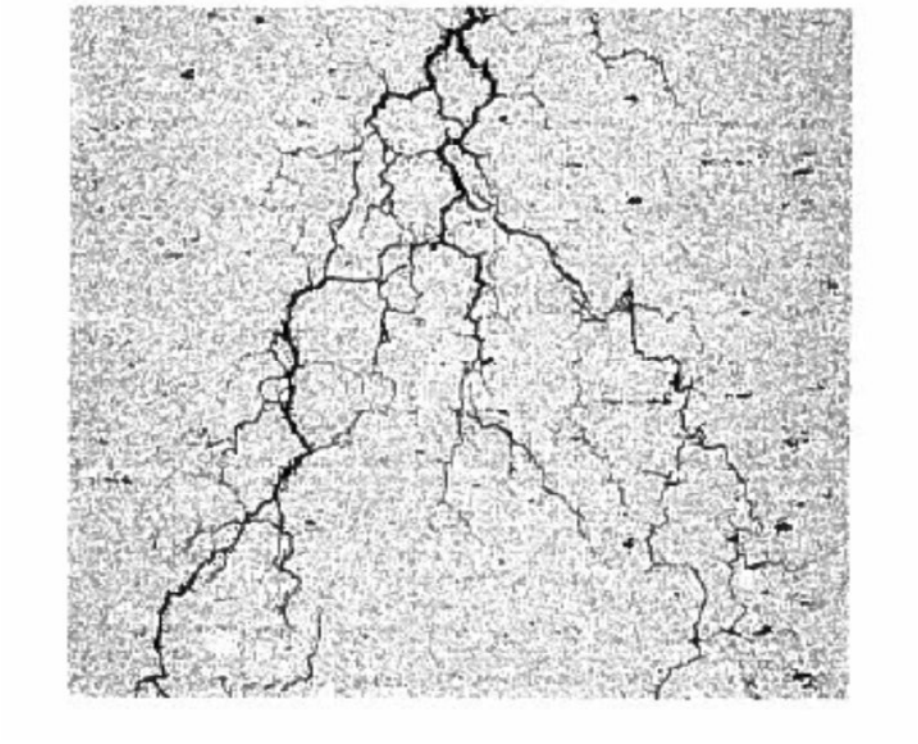


Figure 3-15-9—Micrograph showing intergranular caustic SCC in an expansion joint bellows constructed of Alloy 625 in a 400 psig steam superheater. (Reference 4)

Figure 3-15-10—Micrograph showing transgranular caustic SCC in Alloy 825. Magnification 200X. (Reference 5)

3.16 Cavitation

3.16.1 Description of Damage

a) Cavitation is a form of wear caused by the formation and instantaneous collapse of innumerable tiny vapor bubbles.

b) The collapsing bubbles exert severe localized impact forces that can result in metal loss. (Figure 3-16-1)

c) The bubbles may contain the vapor phase of the liquid, air, or other gas entrained in the liquid medium.

3.16.2 Affected Materials

Most common materials of construction including copper and brass, cast iron, carbon steel, low-alloy steels, 300 series SS, 400 series SS, and nickel-based alloys can be affected by cavitation, although certain materials have greater resistance than others.

3.16.3 Critical Factors

a) In a pump, the difference between the actual pressure or head of the liquid available (measured on the suction side) and the vapor pressure of that liquid is called the net positive suction head (NPSH) available. The minimum head required to prevent cavitation with a given liquid at a given flow rate is called the NPSH required. Inadequate NPSH can result in cavitation.

b) Temperatures approaching the boiling point of the liquid are more likely to result in bubble formation than lower-temperature operation.

c) The presence of solid or abrasive particles is not required for cavitation damage but will accelerate the damage.

d) Cavitation taking place in a corrosive environment can be accelerated by the corrosive effects of the environment. This is often referred to as cavitation-corrosion.

3.16.4 Affected Units or Equipment

a) Cavitation is most often observed in pump casings, pump impellers (low-pressure side), and in piping downstream of orifices or control valves.

b) Damage can also be found in restricted-flow passages or other areas where turbulent flow is subjected to rapid pressure changes within a localized region. Examples of affected equipment include heat exchanger tubes, venturis, and seals.

3.16.5 Appearance or Morphology of Damage

a) Cavitation damage generally looks like sharp-edged pitting but may also have a gouged appearance in rotational components. Damage is typically localized to the cavitation zone. (Figure 3-16-2 to Figure 3-16-5)

b) Cavitating pumps or downstream of control valves may sound like pebbles are tumbling or rattling inside and are typically accompanied by higher vibrations.

3.16.6 Prevention/Mitigation

a) A mechanical modification or design or operating change is usually required in order to fix a cavitation problem. Resistance to cavitation damage may not be significantly improved by a material change. However, wear-resistant alloys and ceramic coatings can help improve cavitation resistance in some situations.

b) Cavitation is best prevented by avoiding conditions that allow the absolute pressure to fall below the vapor pressure of the liquid. Changing the material may also help. Examples of steps that can be taken include:

1. streamlining the flow path to reduce turbulence;
2. decreasing fluid velocities;
3. removing entrained air;
4. increasing the suction pressure of pumps while reviewing the pump efficiency curve;
5. altering the fluid properties, perhaps by adding additives;
6. using hard surfacing or hardfacing; or
7. using a harder and/or more corrosion-resistant material.

c) When attack is accelerated by the mechanical disruption of protective layers or films on the metal surface, such as a protective corrosion scale or inhibitor film, changing to a more corrosion-resistant material may be beneficial. However, changing to a higher hardness version of the same or a similar material in this situation may not improve cavitation resistance. In addition, excessively hard materials may not be suitable if they lack the toughness required to withstand the high local pressures and impact (shear loads) of the collapsing bubbles.

3.16.7 Inspection and Monitoring

a) VT of suspect areas, including use of a boroscope if direct access is not available, can often identify cavitation damage. Typically, the inspection is performed during plant shutdowns.

b) UT, including manual UT scanning and/or AUT, can be used for measuring remaining thickness at damaged areas if the damaged area is large enough and smooth enough for UT to be effective. However, since the damage is normally highly localized, it might be difficult to pinpoint the location of the damage.

1. It can be difficult to get accurate thickness readings on pump casings or other castings due to their inherent thickness variability combined with the fact that inside and outside surfaces may not be parallel.

c) RT can be used to quantify thickness loss in affected components if accessibility allows. Pitting location and depth are measured with quantitative radiographic techniques.

d) Acoustic monitoring of turbulent areas can detect characteristic sound frequencies associated with cavitation. The technique is a qualitative method to determine damage progression.

e) Other techniques include monitoring of fluid properties to find locations of highly turbulent flow.

3.16.8 Related Mechanisms

Erosion and erosion-corrosion (3.27).

3.16.9 References

1. “Evaluation of Erosion and Cavitation,” *Metals Handbook—Corrosion*, Volume 13, 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.

3. V.R. Pludek, *Design and Corrosion Control*, Macmillan Press, 1979.

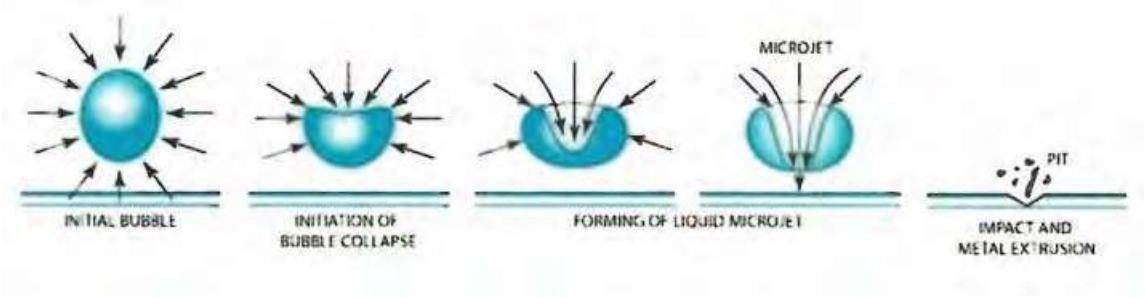


Figure 3-16-1—Mechanism of cavitation damage. As vapor bubbles collapse, microjets form that result in high forces that damage the equipment.

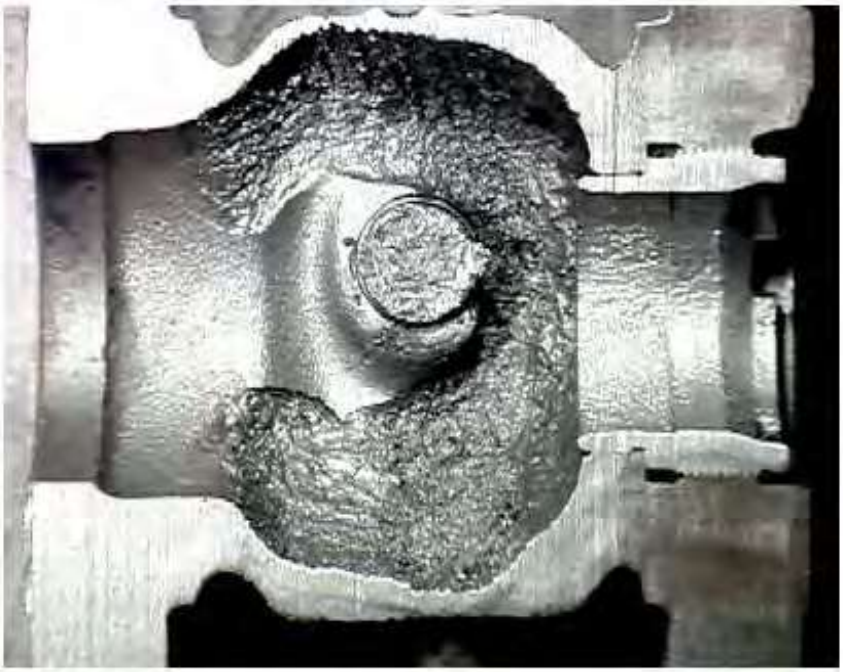


Figure 3-16-2—Cutaway of a CS butterfly valve with cavitation damage after 2 years of service due to a high pressure drop across the valve in a hydrocarbon drain line off a cold low-pressure separator in an atmospheric resid desulfurizing unit.

Figure 3-16-3—Closer view of the damaged surface of the butterfly valve in Figure 3-16-2.

Figure 3-16-4—Cavitation pitting on the low-pressure side of a stainless steel pump impeller.

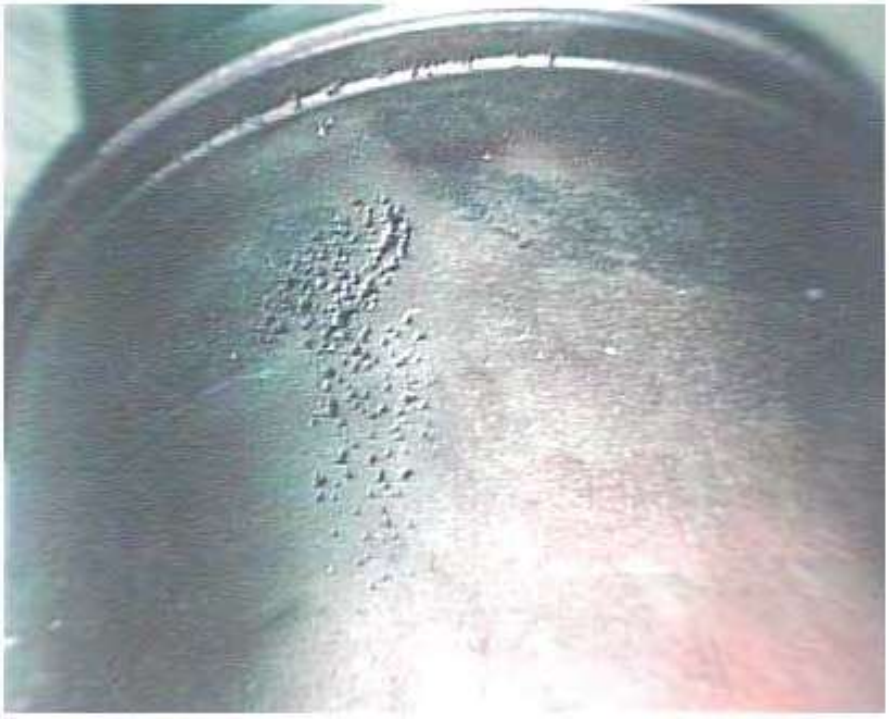


Figure 3-16-5—Pitting caused by cavitation on the water side of a cast iron cylinder liner in a large engine.

3.17 Chloride Stress Corrosion Cracking

3.17.1 Description of Damage

Surface initiated cracking of 300 series SS and some nickel-based alloys under the combined action of tensile stress, temperature, and an aqueous chloride environment. It is also referred to as chloride cracking.

3.17.2 Affected Materials

a) All 300 series SS are highly susceptible. Welds in 300 series SS normally contain some ferrite, producing a duplex structure that is usually more resistant to chloride stress corrosion cracking (Cl^- SCC) than the base metal.

b) Duplex stainless steels are more resistant but still susceptible.

c) Nickel-based alloys are highly resistant but not immune.

3.17.3 Critical Factors

a) Chloride content, temperature, pH, tensile stress, presence of oxygen, and alloy composition are critical factors.

b) Cl^- SCC is caused by the inorganic chloride ion (Cl^-) (or other inorganic halide ions such as bromide, in which case it might be named differently). Organic chlorides will not directly cause Cl^- SCC, but they can, and typically do, produce ionic, inorganic chlorides by the processes of hydrolysis or thermal decomposition (pyrolysis). Therefore, organic chlorides can lead to Cl^- SCC.

c) Increasing levels of chloride increase the likelihood of cracking.

1. No practical lower limit for chlorides exists because of the potential for chlorides to concentrate. For example, heat transfer conditions, as on the surface of exchanger tubes, significantly increase cracking potential. Repetitive wetting and drying situations, including alternating steam and water, can also lead to cracking.

2. Non-condensing systems will be a particular concern, because the chlorides cannot be removed with the water phase.

d) Increasing temperatures increase the potential for cracking, as long as the other required elements (stress and aqueous chloride solution) are present concurrently.

1. Although there are exceptions at lower temperatures and even ambient temperature, particularly with highly cold worked or sensitized materials, cracking usually occurs at metal temperatures above about 140 °F (60 °C), and experience has shown this to be a useful temperature limit guideline for fixed equipment in the refining industry.

e) The potential for cracking increases at lower pH; however, SCC usually does not occur at pH values below 2. At these lower pH values, uniform corrosion generally predominates. Cl^- SCC tendency decreases toward the alkaline pH region; however, stainless steels and some nickel-based alloys (e.g. Alloy 800 and Alloy 825) can suffer caustic SCC in alkaline environments. (See 3.15.)

f) The tensile stress may be applied or residual. The most common area of concern is non-stress-relieved welds. However, highly stressed or cold worked components, such as expansion bellows, are also highly susceptible to cracking.

g) Oxygen dissolved in the water normally accelerates SCC, but it is not clear whether there is an oxygen concentration threshold below which Cl^- SCC does not occur. Other oxidizers in addition to oxygen (e.g. CO and CO_2) can also enhance Cl^- SCC.

h) Nickel content of the alloy has a major effect on resistance. The greatest susceptibility occurs in stainless steels with a nickel content of 8 % to 12 %.

1. Alloys with nickel contents above 35 % are highly resistant, and alloys above 45 % are nearly immune in refining applications, but cracking can still occur in severe conditions.

2. Low-nickel stainless steels, such as the duplex (ferrite-austenite) stainless steels, have improved resistance over the 300 series SS but are not immune.

3.17.4 Affected Units or Equipment

a) Most non-stress-relieved 300 series SS piping and equipment in any process unit are susceptible to Cl^- SCC. Even if the process side will not cause SCC, if the piping or equipment operates above 140 °F (60 °C), it is likely exposed to alternating wet and dry conditions on the outside.

b) Chloride cracking has occurred in water-cooled condensers and on the process side of crude tower overhead condensers.

c) Stainless steel drains in hydroprocessing units are susceptible to cracking, particularly during start-up, if not properly purged.

d) Bellows and instrument tubing, particularly those associated with hydrogen recycle streams contaminated with chlorides, can be affected.

e) External Cl^- SCC can occur on insulated 300 series SS surfaces when insulation gets wet.

1. The operating temperature range of most concern for external Cl^- SCC is 140 °F (60 °C) to 400 °F (205 °C).

f) Chloride cracking has occurred in boiler drain lines.

g) Highly localized Cl^- SCC has occurred in exchanger tube bundles where the bulk fluid temperature inside the tubes was above the water dew point. Cold fluid entering the shell side caused shock condensation within the tubes and resultant chloride cracking on the tube side.

h) Units processing or co-processing bio-based or renewable feedstocks (biomass, natural fats and oils, etc.) are particularly susceptible to Cl^- SCC due to high levels of organic chlorides converting to inorganic chlorides in the reactor effluent.

3.17.5 Appearance or Morphology of Damage

a) Surface-breaking cracks can occur from the process side or externally under insulation. (Figure 3-17-1 and Figure 3-17-2)

b) The component usually shows no visible signs of corrosion.

c) Characteristic stress corrosion cracks have many branches and may be visually detectable as spider web or craze cracking on the surface. (Figure 3-17-3)

d) Metallography of cracked samples typically shows branched, transgranular cracks. (Figure 3-17-4 to Figure 3-17-6)

e) Cracking of sensitized 300 series SS may be intergranular.

f) Cl^- SCC in nickel-based alloys, which can occur under severe conditions, appears similar to Cl^- SCC in stainless steel. (Figure 3-17-7)

g) Fracture surfaces typically have a brittle appearance.

3.17.6 Prevention/Mitigation

a) Materials of construction resistant to Cl^- SCC should be used. Carbon steels, low-alloy steels, and 400 series SS are not susceptible to Cl^- SCC.

b) When hydrotesting, low-chloride-content water should be used, followed quickly by thorough dryout.

c) A suitable coating should be applied to stainless steel piping and equipment prior to insulating.

1. Shrink-wrapped PVC labels, coatings, or label adhesives with high levels of chlorides or other halogen ions should be avoided.

d) Avoid designs that create stagnant regions where chlorides can deposit or concentrate.

e) Although not a standard or common refining industry practice, a suitable high-temperature stress relief of 300 series SS after fabrication will reduce residual stresses. However, consideration should be given to the possible effects of sensitization that may occur, increasing susceptibility to PTA SCC (3.52), possible distortion problems, and the potential for stress relaxation cracking (SRC) (3.54).

f) Avoid exchanger designs with 300 series SS steel tubes and a high delta T between the shell and tube side where localized condensation can occur on or in the tubes.

g) Avoid contact with high-chloride water run-off that can occur with the use of salts for snow and ice melting.

3.17.7 Inspection and Monitoring

Cracking may be either process side or external (usually under insulation that has become wet or where external water can collect), and it should be understood on which side the damage is occurring in order to properly develop an inspection plan. Cl^- SCC may be detected using the following methods.

a) VT can be used to find advanced stages of cracking.

b) PT can be used for Cl^- SCC. However, extremely fine cracks may be difficult to detect with PT. Special surface preparation methods, including polishing or high-pressure water blast, may be required in some cases, especially in high-pressure services.

c) ECT inspection methods can be used on condenser tubes as well as piping and pressure vessels.

d) Angle beam UT (SWUT and PAUT) from the opposite wall can be used for crack detection; however, detection and characterization of the cracking will be difficult due to the craze-cracked, multi-branched appearance of Cl^- SCC.

e) RT is often not sensitive enough to detect cracks except in advanced stages where a sufficient network of cracks has developed.

3.17.8 Related Mechanisms

Caustic SCC (3.15), PTA SCC (3.52), and brine corrosion (3.10).

3.17.9 References

1. 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. 88–90.

2. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, pp. 111–123.

3. *Focus on Chloride Stress Corrosion Cracking (CSCC) of 300 Series Stainless Steels*, MTI Technical Awareness Bulletin No. 8, Materials Technology Institute, St. Louis, MO, 2012.

4. D.R. McIntyre and C.P. Dillon, *Guidelines for Preventing Stress Corrosion Cracking in the Chemical Process Industries*, MTI Publication No. 15, Materials Technology Institute, St. Louis, MO, 1985.

Figure 3-17-1—External cracking of Type 304 SS instrument tubing under insulation.

Figure 3-17-2—External cracking of Type 304 SS instrument tubing under insulation.

Figure 3-17-3—Cracking on the shell side of a Type 316L SS tube in steam service at 450 °F (230 °C) showing tight cracks with a crazed or spider web appearance.

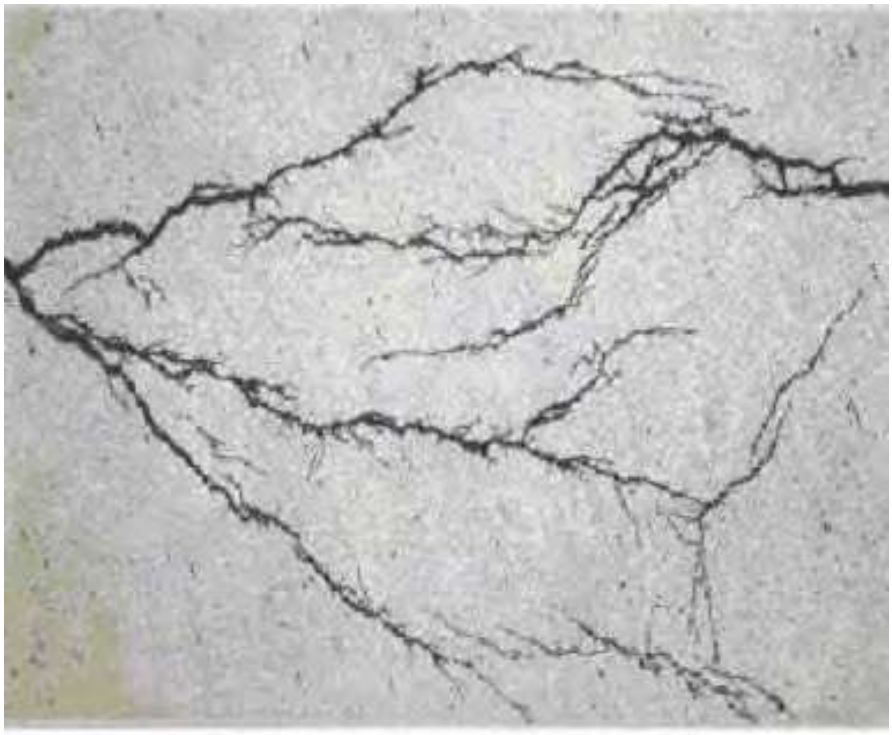


Figure 3-17-4—Photomicrograph of a cross section of the tube in Figure 3-17-3 showing fine branching cracks. (Magnification 50X, unetched.)

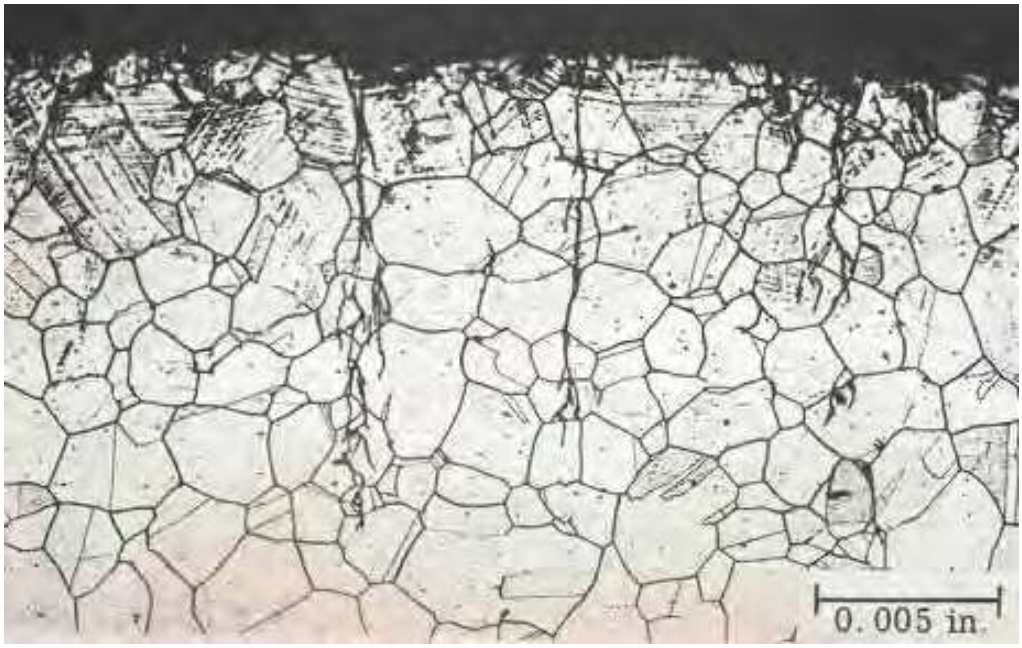
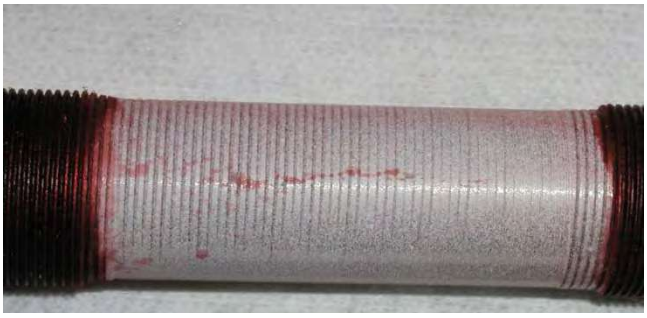
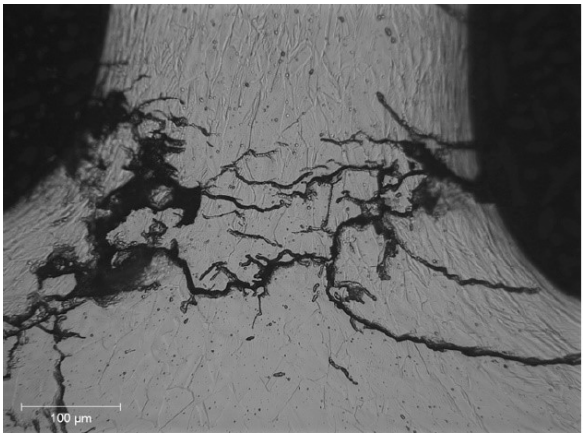


Figure 3-17-5—Another photomicrograph of a cracked tube illustrating the transgranular mode of cracking initiating at the surface. (Etched.)

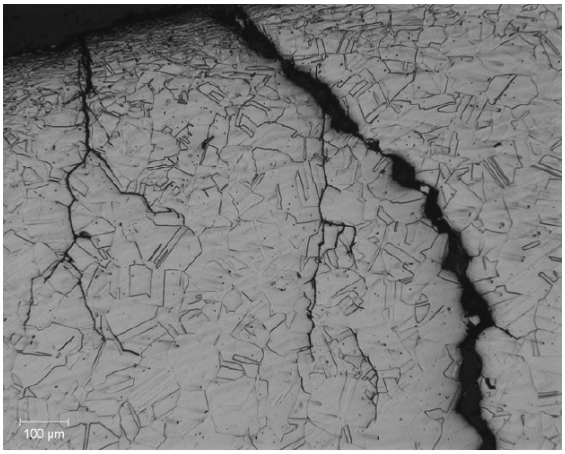
Figure 3-17-6—Cl^- SCC on the thread surface of a failed 303 SS bolt.



(a)



(b)



(c)

Figure 3-17-7—Severe cracking of a finned Alloy C-276 tube in a deethanizer reboiler after 8 years of service due to ammonium chloride carryover. (a) Hundreds of cracks initiated on the OD (process side) of the tube. (b) The cracks were associated with the cold-worked portion of the tubes at the fins. (c) The cracks were branching and transgranular, typical of Cl^- SCC.

3.18 CO_2 Corrosion

3.18.1 Description of Damage

CO_2 corrosion results when CO_2 dissolves in water to form carbonic acid (H_2CO_3). The acid may lower the pH, and sufficient quantities may promote general corrosion and/or pitting corrosion of carbon steel.

3.18.2 Affected Materials

Carbon steel and low-alloy steels are affected. Increasing the level of chromium in steels offers no major improvement in resistance until a minimum of 12 % Cr is reached, i.e. Type 410 SS. 300 series austenitic SS is highly resistant to CO_2 corrosion.

3.18.3 Critical Factors

a) Liquid water must be present for CO_2 corrosion to occur. Beyond that, the partial pressure of CO_2, pH, temperature, oxygen contamination, and velocity are critical factors.

b) Increasing partial pressures of CO_2 result in lower pH and, therefore, higher rates of corrosion.

c) Corrosion occurs in the liquid water phase, often at locations where CO_2 condenses from the vapor phase.

d) Increasing temperatures increase corrosion rate up to the point where CO_2 is driven off.

e) Oxygen can accelerate corrosion rates. Oxygen should be limited to 10 ppb to avoid accelerating corrosion

f) High velocity and turbulence can cause accelerated, localized corrosion.

3.18.4 Affected Units or Equipment

a) BFW and condensate systems in all units are affected.

b) Effluent gas streams off the shift converters in hydrogen plants can be affected. Corrosion usually occurs when the effluent stream drops below the dew point at approximately 300 °F (150 °C). Corrosion rates as high as 1000 mpy have been observed.

c) Overhead systems of regenerators in CO_2 removal plants are affected.

d) Stripping steam is commonly used in crude towers, and so CO_2 corrosion can occur in the overhead system where the dew point is reached.

e) Locations where high velocity, impingement, or turbulence can create increased susceptibility include areas downstream of control valves, and changes in piping direction (e.g. at elbows and tees) or piping diameter (i.e. at reducers).

f) Corrosion may occur along the bottom surface of a pipe if there is a separate water phase or along the top surface of a pipe if condensation in wet gas systems occurs.

g) Locations where a cooling effect can cause condensation and resultant CO_2 (carbonic acid) corrosion include where insulation is damaged, where portions of blind flanged nozzles extend beyond the insulation and thus cool below the dew point, and where pipe supports attach to piping. (Figure 3-18-1 and Figure 3-18-2)

3.18.5 Appearance or Morphology of Damage

a) The appearance can differ depending on the unit and equipment in which it occurs (steam and condensate systems vs H_2 manufacturing units vs crude tower overheads vs CO_2 removal plants vs oilfield production equipment). Contributing to the differences in appearance are the type of water (BFW or steam condensate vs untreated fresh water vs salt water or brine) and the other species in the water, e.g. oxygen, H_2S, and other acids and salts.

b) Localized general thinning and/or pitting corrosion normally occurs in carbon steel. (Figure 3-18-3 to Figure 3-18-5)

c) Corrosion generally occurs or is worse in areas of turbulence and impingement. It is sometimes seen at the root of piping welds.

1. Carbon steel may suffer deep pitting, grooving, or smooth “wash out” in areas of turbulence.

d) Corrosion may initiate where water first condenses and may be most severe at water/vapor interfaces.

e) It may appear as a number of flat-bottomed pits, sometimes called “mesa”-type pitting. (Figure 3-18-6)

3.18.6 Prevention/Mitigation

a) Corrosion inhibitors can reduce CO_2 corrosion in steam condensate systems. Vapor phase inhibitors may be required to protect against condensing steam.

b) Increasing condensate pH above 6 can reduce corrosion in steam condensate systems.

c) 300 series SS are highly resistant to CO_2 corrosion in most applications. 400 series SS and duplex stainless steel are also resistant.

d) Selective upgrading to stainless steel is usually required in operating units designed to produce and/or remove CO_2 (i.e. hydrogen plants and CO_2 removal units). Selecting a stainless steel to mitigate CO_2 corrosion in any operating unit needs to account for other potential damage mechanisms applicable to the specific environment.

e) CO_2 corrosion in steam condensate systems can often be managed by correcting or improving the operating conditions and/or water treatment program.

f) Ensure insulation and jacketing are in good condition to prevent unexpected and undesired cooling, which could lead to condensation and resultant CO_2 corrosion.

g) Internal coatings can be effective where the design and environment permit.

3.18.7 Inspection and Monitoring

a) VT, UT, and RT (preferably profile RT) can be used for general and local loss in thickness where water wetting is anticipated.

1. The use of remote video probes can be effective for locations with limited or no direct line-of-sight (e.g. in boiler tubes).

b) Preferential corrosion of welds may require angle beam UT (SWUT or PAUT) or RT.

c) Permanently mounted thickness monitoring sensors can be used.

d) Monitor water analyses (pH, Fe, O_2, etc.) to determine changes in operating conditions.

3.18.8 Related Mechanisms

Boiler water condensate corrosion (3.9) and carbonate cracking (3.12).

3.18.9 References

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

2. L. Garverick, *Corrosion in the Petrochemical Industry*, ASM International, Materials Park, OH, 1994.

3. H.M. Herro and R.D. Port, *The Nalco Guide to Cooling Water System Failure Analysis*, McGraw-Hill, New York, NY, 1991, pp. 259–263.

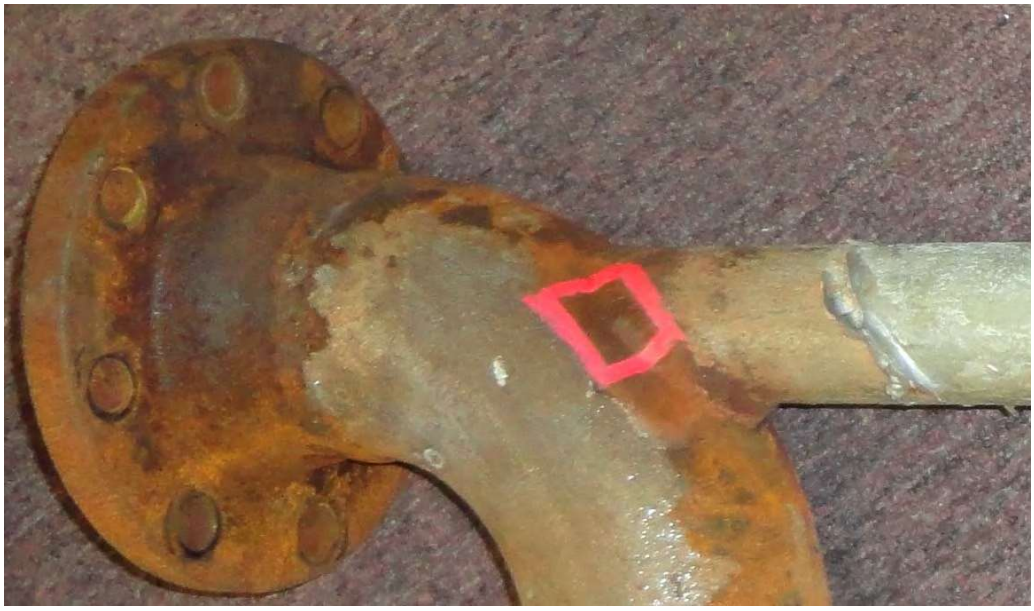


Figure 3-18-1—CO_2 corrosion caused a leak in an elbow at a support leg. The cooling effect of the support leg caused carbonic acid to condense from the vapor phase.

Figure 3-18-2—Corrosion found on the inside of the elbow in Figure 3-18-1.

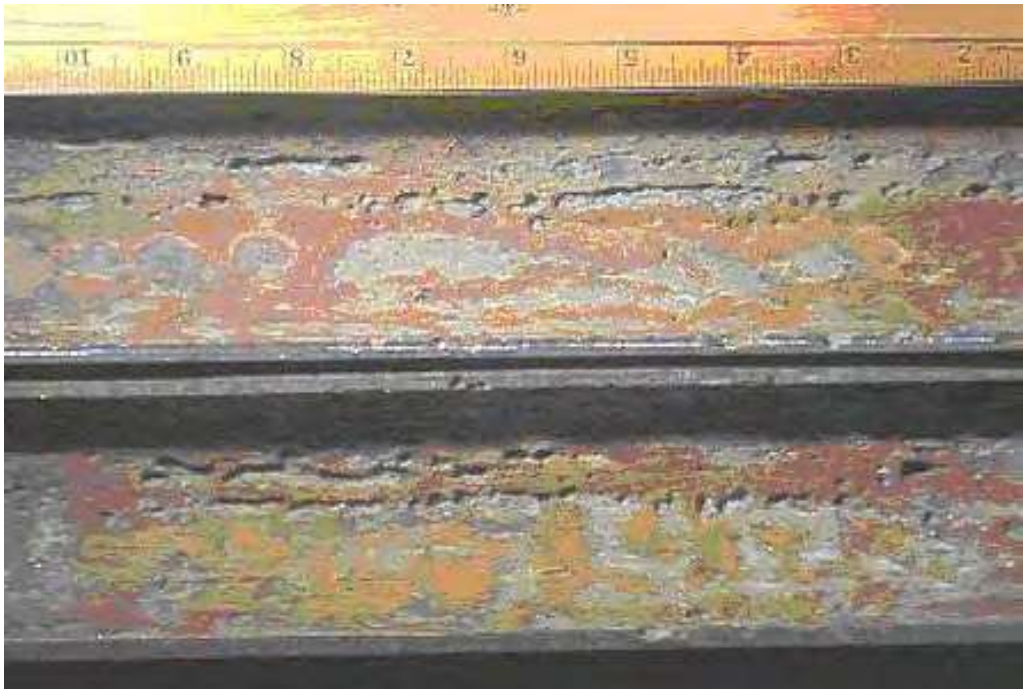


Figure 3-18-3—CO_2 corrosion of a carbon steel oil and gas production flow line.

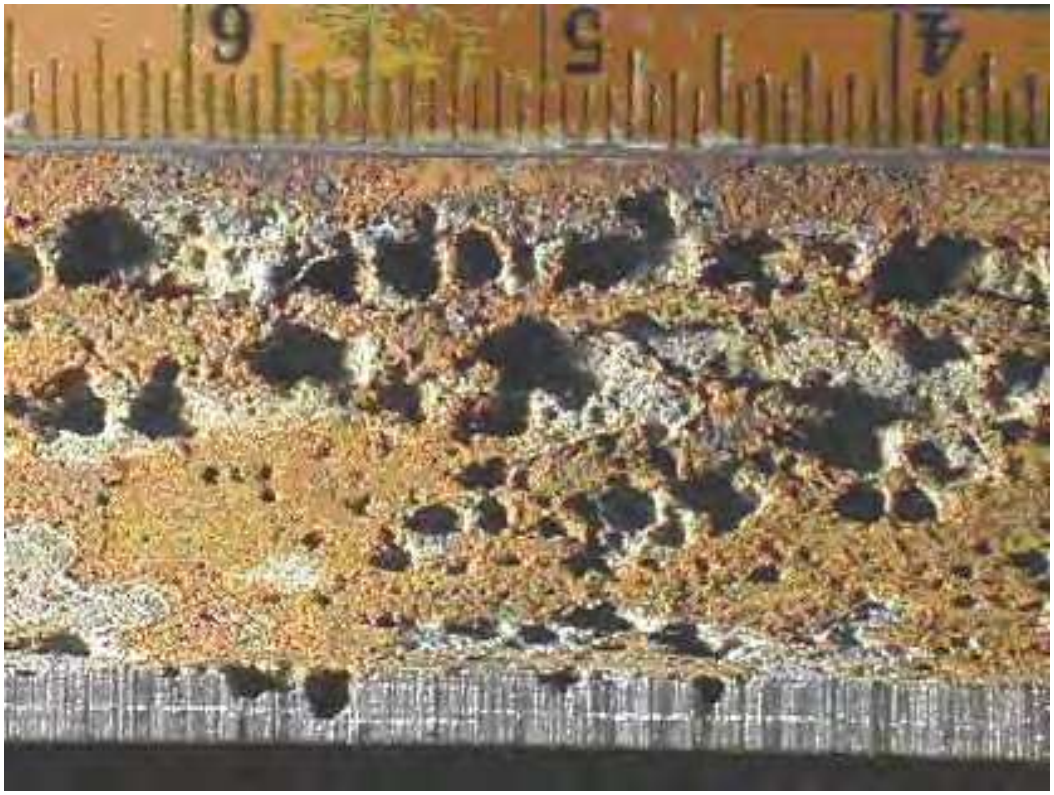


Figure 3-18-4—Higher-magnification view of the corrosion pits in Figure 3-18-3.

Figure 3-18-5—CO_2 corrosion of a carbon steel pipe nipple in CO_2-contaminated water.

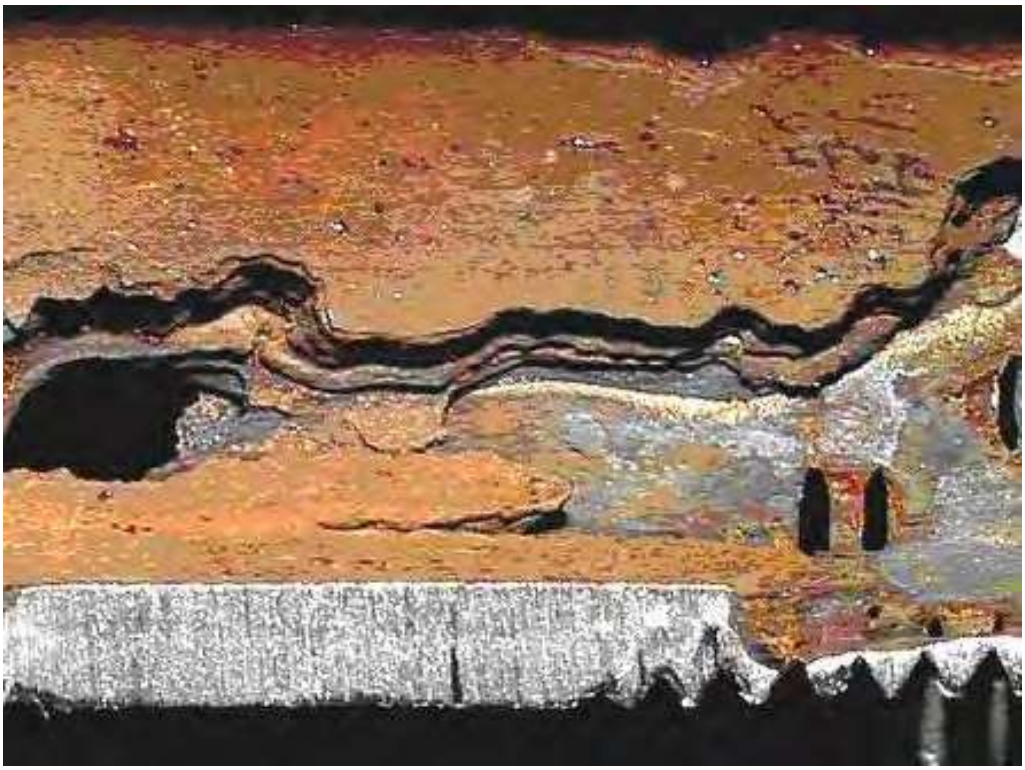


Figure 3-18-6—A view inside the nipple in Figure 3-18-3 showing "mesa"-type corrosion.

3.19 Concentration Cell Corrosion

3.19.1 Description of Damage

Concentration cell corrosion is not a separate corrosion mechanism but rather provides an explanation for or has an influence on a number of commonly occurring corrosion phenomena, including under-deposit corrosion, crevice corrosion, contact point corrosion (also called touch point corrosion), soil/air interface corrosion (see 3.57), and CUI (see 3.22).

3.19.2 Affected Materials

Susceptibility to concentration cell corrosion correlates to the overall aqueous corrosion resistance of the material. Carbon steel is the most susceptible and the most commonly used material in the situations where these phenomena occur in refining. Low-alloy steels and stainless steels are also susceptible, with degree of susceptibility depending on the chemical composition of the alloy and the aggressiveness of the environment. Higher-alloy materials including high-Cr ferritic stainless steels, austenitic super stainless steels, super duplex stainless steels, and Ni-Cr-Mo alloys, as well as titanium and its alloys, have good to excellent resistance to concentration cell corrosion in refining applications.

3.19.3 Critical Factors

a) Concentration cell corrosion occurs in aqueous environments. It involves an *occluded cell* surrounded by an environment with a slightly different composition. The occluded cell is the area beneath the deposit, inside the crevice, where the pipe sits on its support, the first few inches of soil beneath the ground surface, or where pipe is contacted by wet insulation. In most cases, the difference between the environment in the occluded cell and the area around it is the oxygen concentration. Because the oxygen within the occluded cell gets depleted by the initial corrosion that occurs, the area outside the occluded cell has a higher oxygen concentration than that within the occluded cell. This *differential aeration cell*, or *oxygen concentration cell*, causes the lower-oxygen area to corrode preferentially to the higher-oxygen area. It is essentially a galvanic couple where the low-oxygen area is the anode and the higher-oxygen area is the cathode.

b) Concentration cell corrosion can also occur in the absence of air or oxygen, such as under deposits laying at the bottom of a tower or vessel, or along the bottom of a horizontal run of piping in a refinery process unit where there is presumably no air or oxygen present during operation. In this case, if there is under-deposit corrosion, it is due to a chemical species other than oxygen, perhaps sulfur or chlorides.

c) Crevice corrosion in 300 series SS and similar alloys is related to the chloride content of the environment as well as the pH and temperature. It is closely related to the chloride pitting phenomenon in these materials. In addition to a contribution from the differential aeration cell created between the area within the crevice and the area outside it, the pH within the crevice decreases as the corrosion proceeds, by a process called metal ion hydrolysis, thereby further accelerating the corrosion rate.

    1. Resistance to chloride crevice corrosion (and chloride pitting) of stainless steels is related to the amount of Cr and Mo, as well as certain other chemical additions, in the alloy. It is typically represented by the PREN, which quantifies the material's expected resistance based on chemical composition. [See *Brine Corrosion* (3.10) for further discussion of PREN.]

d) In order for concentration cell corrosion to occur, a potentially corrosive aqueous environment must exist. The presence of a concentration cell generally accelerates the corrosion that would otherwise occur at a slower rate without the concentration cell, in the same way that a galvanic couple accelerates the corrosion on the more anodic material when placed in a potentially corrosion-causing environment but does not create a new corrosion mechanism by itself. The corrosion rate under the deposit or within the crevice occurs at an accelerated rate compared to the corrosion occurring outside the deposit or crevice. The corrosion at the contact point where the pipe sits on its support is accelerated compared to the atmospheric (and water) corrosion occurring on the rest of the pipe. The soil corrosion at the soil/air interface is accelerated by the oxygen differential between the first few inches of soil and the air above it. If there is no corrosive environment within and surrounding the occluded cell, e.g. in clean, water-free hydrocarbon, there will not be corrosion beneath any deposits, either (assuming no MIC). Similarly, even corrosive salt deposits such as ammonium

chloride will not cause corrosion until they become water-wet and thereby create an acidic, corrosive environment beneath the deposit.

3.19.4 Affected Units or Equipment

a) All process and utility piping and equipment in a refinery is potentially susceptible to concentration cell corrosion, either on the inside, the outside, or both.

b) Anywhere deposits (sludge, scale, salts, etc.) form within the piping or equipment is a potential site for under-deposit corrosion.

c) Equipment internals that are bolted together, e.g. tray components in towers, as well as baffle holes through which tubes pass in heat exchangers, flange and gasket faces, and close-fitting components in valves and instruments are potential locations where crevice corrosion might occur.

d) Deposits forming on the outside of piping or equipment, e.g. dirt piling up beneath low lying piping or sloughing off of road crossings and then covering exposed bare pipe running beneath the crossing, can lead to under-deposit corrosion, which, in this example, could also be categorized as soil corrosion or soil/air interface corrosion.

e) Loose, peeling coatings can trap moisture, dirt, or other debris and create an under-deposit or crevice corrosion condition.

f) Everywhere a pipe is supported by a saddle, sits on a beam, or is not in some way supported using a method to preclude contact point corrosion is a potential site for accelerated atmospheric corrosion. The situation is made worse if dirt or other materials can get trapped and contained within the contact area.

g) See also ammonium bisulfide corrosion (3.5), ammonium chloride corrosion (3.6), atmospheric corrosion (3.8), brine corrosion (3.10), cooling water corrosion (3.20), CUI (3.22), fuel ash corrosion (3.30), galvanic corrosion (3.31), MIC (3.45), oxygenated water corrosion (3.49), soil corrosion (3.57), and SW corrosion (acidic) (3.58).

3.19.5 Appearance or Morphology of Damage

As with most corrosion situations in refining, concentration cell corrosion will typically result in an unevenly corroded surface often described as pitting. Crevice corrosion in austenitic stainless steels due to chlorides is typically an accumulation of sharp, narrow, deep pits. See the mechanisms in 3.58.4 g), above, for more specific descriptions.

3.19.6 Prevention/Mitigation

a) Most situations dictate that an upgrade of material, most commonly from carbon steel, is not a practical or economic alternative.

b) Keeping dirt and other deposits from building up against or beneath equipment will prevent this type of attack.

c) Taking practical steps to minimize deposit, sludge, and scale formation in operating units will mitigate the damage.

d) Pipe supports can be designed to eliminate the ability to trap dirt and moisture between the pipe and its support, e.g. by using fully welded contact points.

e) Coatings can be used to protect steel equipment likely to become exposed to dirt or other debris buildup.

f) Peeling coatings should be repaired.

g) Where a materials upgrade is a reasonable solution to a crevice corrosion or under-deposit corrosion concern, e.g. where 300 series SS is commonly used or where process salt deposits are a concern, consider an upgrade to an appropriate, more corrosion-resistant alloy.

3.19.7 Inspection and Monitoring

a) VT is the method most commonly used when access to the corroded surface is available. Pit gaging is often applied along with VT to measure the depth of the attack. Laser scanning and/or structured white light imaging with pit gages can also be performed.

b) UT thickness measurements from the surface opposite the attack can be used to measure remaining wall thickness.

c) UT scanning methods (e.g. AUT, manual close-grid, scanning UT) may be needed to assess large surfaces such as the bottom of a tower or vessel, i.e. by scanning from the underside to determine the amount of damage caused by deposits on the inside. Short-range (high-frequency) GWT techniques may also be used to detect wall loss.

d) If the cause of the corrosion cannot be eliminated, permanently mounted thickness monitoring sensors can be used.

e) The presence of deposits in heat exchangers can sometimes be detected by an increase in pressure drop or if the thermal performance of exchangers has deteriorated.

3.19.8 Related Mechanisms

Ammonium bisulfide corrosion (3.5), ammonium chloride corrosion (3.6), atmospheric corrosion (3.8), brine corrosion (3.10), cooling water corrosion (3.20), CUI (3.22), fuel ash corrosion (3.30), galvanic corrosion (3.31), MIC (3.45), oxygenated water corrosion (3.49), soil corrosion (3.57), and SW corrosion (acidic) (3.58).

3.19.9 References

None.

3.20 Cooling Water Corrosion

3.20.1 Description of Damage

General or localized corrosion of carbon steels and other metals caused by dissolved salts, gases, organic compounds, or microbiological activity in cooling water systems.

3.20.2 Affected Materials

Carbon steel, all grades of stainless steel, copper and copper alloys, aluminum and aluminum alloys, titanium, and nickel alloys.

3.20.3 Critical Factors

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

b) Higher cooling water temperature causes increased corrosion rates.

   1. Increasing cooling water heat exchanger outlet temperatures and or process-side inlet temperatures tend to increase exchanger bundle corrosion rates as well as fouling tendency. If the process-side temperature is above 140 °F (60 °C), a scaling potential exists with fresh water and becomes more likely as process temperatures increase and as cooling water inlet temperatures rise. Brackish and salt water outlet temperatures above about 115 °F (45 °C) may cause serious scaling.

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

d) Fouling may be caused by mineral deposits (hardness), silt, suspended organic materials, corrosion products, mill scale, and marine and microbiological growth.

e) Low velocities can promote increased corrosion. Velocities should be high enough to minimize fouling and dropout of deposits but not so high as to cause erosion. Velocity limits depend on the pipe diameter or heat exchanger tube material and water quality.

   1. Oversized channel heads, water side exchanger shells, or dead-legs can be areas of low or stagnant flow.

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

f) High velocities can also lead to accelerated corrosion.

   1. Exchanger tubes can see a dramatic increase in flow velocity.

g) 300 series SS, depending on the specific alloy and the water and metal temperatures, can suffer pitting and crevice corrosion. At temperatures above about 140 °F (60 °C), 300 series SS can also suffer Cl^- SCC even in freshwater systems where a chloride salt concentrating mechanism is in place. This is a particular concern with the tubes in water-cooled heat exchangers, i.e. condensers and coolers. (See 3.17.)

h) Brass (Cu-Zn) alloys can suffer dezincification in fresh, brackish, and salt water systems. They can also suffer SCC if any ammonia or ammonium compounds are present in the water or on the process side if cross-leakage occurs.

i) ERW carbon steel pipe or exchanger tubes may suffer severe weld and/or HAZ corrosion in fresh or brackish water.

j) When connected to a more anodic material, titanium may suffer severe hydriding embrittlement. Generally, the problem occurs at temperatures above 165 °F (75 °C). (See 3.66.)

3.20.4 Affected Units or Equipment

Cooling water corrosion is a concern with cooling towers, piping, pumps, water-cooled heat exchangers, and any other equipment associated with cooling water systems.

3.20.5 Appearance or Morphology of Damage

a) Cooling water corrosion can result in many different forms of damage including general corrosion, pitting corrosion (Figure 3-20-1), MIC, SCC, and fouling.

b) General or uniform corrosion of carbon steel occurs when dissolved oxygen is present. Many oxidizing biocides also increase this tendency.

c) Localized corrosion may result from under-deposit corrosion, crevice corrosion, or MIC.

d) Wavy or smooth corrosion at nozzle inlets or outlets and exchanger tube inlets may be due to flow accelerated corrosion, erosion, or abrasion.

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

3.20.6 Prevention/Mitigation

a) Cooling water corrosion (and fouling) is best managed by proper design, operation, and chemical treatment of cooling water systems.

b) Process-side inlet temperatures of water-cooled exchangers should be maintained below 140 °F (60 °C).

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

d) The metallurgy of heat exchanger components may need to be upgraded for improved resistance, especially in waters with high chloride content, low velocity, and/or poorly maintained water chemistry, where exchanger process-side temperatures are high, or where there is simply the desire to extend tube life.

e) Periodic mechanical cleaning of tube IDs and ODs should be performed in order to maintain clean heat transfer surfaces.

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

g) Installation of sacrificial anodes on the cooling water side of water-cooled heat exchangers can increase the life of channel heads, tubesheets, and tubes to a certain extent, as long as they are galvanically coupled to the anodes.

3.20.7 Inspection and Monitoring

a) Cooling water should be monitored for process conditions that affect corrosion and fouling, including but not limited to:

1. pH,
2. oxygen content,
3. cycles of concentration,
4. biocide and other chemical residual,

5. biological activity,
6. iron and manganese count,
7. cooling water outlet temperatures,
8. hydrocarbon contamination, and
9. process leaks.

b) Periodic calculation of overall heat exchanger performance (U-factors) will provide information on potential scaling and fouling. These could be an indication that corrosion damage is occurring in the piping, exchanger tubes, and/or other equipment in the system.

c) Strategically placing continuous corrosion monitoring devices on the system, such as corrosion coupons, ER probes, or online monitoring sensors, can provide an early indication of increased corrosion rates that need further evaluation.

d) Areas with sharp reduction or large increases in diameter should be considered for velocity survey locations as velocities that are either too high or too low can dramatically affect the damage rate of the equipment. Several types of flow meters are available that can be used to check the velocity of water in the cooling water system.

e) When water sides of exchangers are opened for inspection, checking the sacrificial anodes (when installed) may indicate the relative corrosivity of the cooling water and if the sacrificial anode has been consumed and needs replacement.

f) Exchanger tube inspection can be used to establish corrosion rates and predict tube life in order to plan for tube or tube bundle repair/replacement. Some nondestructive methods to inspect tubes are as follows.

1. RFT is commonly used for inspection of ferrous (carbon steel) tubes. RFT has an equal sensitivity to ID and OD indications and can detect and size corrosion and pitting as well as baffle cuts.
2. ECT is the preferred method for non-ferromagnetic materials as it has a higher probability of detecting all types of damage than ultrasonic methods.
3. IRIS is used when a higher flaw detection and sizing capability is needed (compared to the other methods), but it is slower, and thorough tube cleaning is required prior to inspection. IRIS can be used on both ferrous and non-ferrous materials. IRIS is most commonly used on carbon steel tubes.

g) A destructive method for evaluation is extracting and splitting representative tubes to gain access to the internal surfaces for direct examination. This method is most often used on failed tubes that require replacement and is useful in determining the cause of the tube failure. It may also be used on tubes where significant damage has been indicated and needs verification. The knowledge gained from this method may aid in tube material selection and can help create mitigation plans to avoid future damage.

3.20.8 Related Mechanisms

Microbiologically induced corrosion (3.45), Cl^- SCC (3.17), galvanic corrosion (3.31), concentration cell corrosion (3.19), and brine corrosion (3.10).

3.20.9 References

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

2. H.M. Herro and R.D. Port, *The Nalco Guide to Cooling Water System Failure Analysis*, McGraw-Hill, New York, NY, 1991, pp. 259–263.

3. NACE SP0189, *Online Monitoring of Cooling Water Systems*, NACE International, Houston, TX.

4. NACE SP0300, *Corrosion of Metals and Alloys—Corrosion and Fouling in Industrial Cooling Water Systems—Part 1: Guidelines for Conducting Pilot-scale Evaluation of Corrosion and Fouling Control Additives for Open Recirculating Cooling Water Systems*, NACE International, Houston, TX.

5. NACE/EFC Joint Publication, *Monitoring and Adjustment of Cooling Water Treatment Operating Parameters*, NACE International, Houston, TX.

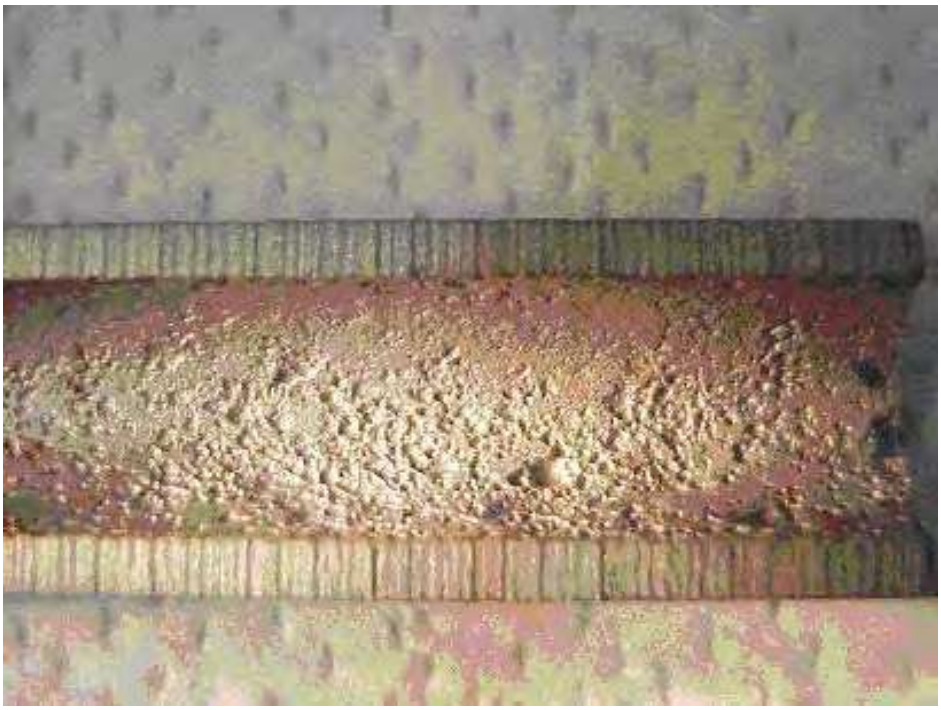


Figure 3-20-1—Cooling water corrosion on the ID of a carbon steel heat exchanger tube operating at 85 °F (30 °C).

3.21 Corrosion Fatigue

3.21.1 Description of Damage

A form of fatigue cracking in which cracks develop under the combined effects of cyclic loading and corrosion. The number of fatigue stress cycles to failure is reduced in a corrosive environment as compared to the number of cycles to failure in the absence of a corrosive environment. Cracking often initiates at a stress concentration such as a pit in the surface. Cracking can initiate at multiple sites.

3.21.2 Affected Materials

All metals and alloys.

3.21.3 Critical Factors

a) The critical factors are the same as those associated with mechanical fatigue (3.43), i.e. cyclic stress level, number and frequency of stress cycles, stress concentration, and material properties, along with the addition of the nature of the corrosive environment.

b) Although corrosion fatigue can occur in the absence of visible or obvious corrosion on the metal surface, in practice, cracking is more likely to occur in environments that promote pitting or localized corrosion.

c) Corrosion fatigue cracking can result from either mechanically induced cyclic stresses or thermally induced cyclic stresses. (See *Mechanical Fatigue*, 3.43, and *Thermal Fatigue*, 3.64.)

d) Contrary to the case with purely mechanical fatigue, there is no endurance limit with corrosion fatigue. Corrosion promotes failure at a lower stress and fewer number of cycles than the materials' normal endurance limit in the absence of corrosion and often results in propagation of multiple parallel cracks.

e) Crack initiation typically occurs at stress concentration locations such as corrosion pits, notches, surface defects, changes in section, or welds, especially fillet welds.

3.21.4 Affected Units or Equipment

Rotating equipment, deaerators, and cycling boilers as well as any equipment subjected to cyclic stresses in a corrosive environment are potentially susceptible to corrosion fatigue cracking. Some examples include the following.

a) Rotating equipment.

   Pump shafts that are not resistant to corrosion in their environment may suffer pitting or other corrosion that will reduce the fatigue life of the shaft. The pitting can act as a stress riser to promote cracking. Galvanic couples between the impeller and the pump shaft may exacerbate the problem. If any other cracking mechanisms such as SCC or SSC are involved, fatigue life may be further reduced.

b) Deaerators.

   In the late 1980s, deaerators in the pulp and paper, refining, petrochemical, and fossil fuel utility industries had major deaerator cracking problems. Cracking is typically associated with welds, especially non-stress-relieved welds, and particularly attachment welds. Complete vessel failures in the pulp and paper industry resulted in a diligent inspection program that found major cracking problems across the various industries. It was concluded that residual welding and fabrication stresses, stress risers (attachments and weld reinforcement), and the normal deaerator environment could produce multiple corrosion fatigue cracking problems.

c) Cycling boilers.

A cycling boiler may see several hundred cold starts over its useful life, which—because of differential expansion—continually cracks the protective magnetite scale, allowing corrosion to continue. This could be described as a case of low-cycle corrosion fatigue as well as cyclic stress enhanced corrosion. It is also referred to as stress-assisted cracking in some references.

d) Other equipment.

While virtually all equipment used in a refinery is subject to corrosion, even if it is only atmospheric corrosion, it is not useful in a practical sense to differentiate in most cases between corrosion fatigue and either mechanical fatigue or thermal fatigue. Most fatigue situations arising in refining can be dealt with by considering the situation as either mechanical fatigue or thermal fatigue, as applicable, without introducing the additional complicating (and mainly academic in this case) issue of corrosion fatigue. Another way of saying this is that all fatigue cracking in a refinery is corrosion fatigue, but unless there is a key contributing factor such as SCC or deep sharp pitting involved, practitioners will generally deal with the situation simply as either mechanical fatigue or thermal fatigue. In most cases, even without any contribution from corrosion, the mechanical or thermal fatigue cracking was going to occur anyway.

3.21.5 Appearance or Morphology of Damage

a) The fatigue fracture surface will appear brittle, and the cracks will be relatively straight, transgranular, and unbranched. There may be multiple parallel cracks.

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

c) In rotating equipment, cracking is generally straight and transgranular with minimal branching.

d) In deaerators and deaerator storage tanks, cracking is surface breaking to the interior of the vessel. The cracks may or may not be tight in appearance and may be tightly filled with corrosion by-products. Pitting is often a precursor to and the initiation site for cracking.

e) In cycling boilers, the damage usually appears first on the water side of buckstay (structural) attachments. (Figure 3-21-1 to Figure 3-21-5) The cracking pattern may be circular cracks surrounding the weld between the buckstay attachment and the waterwall tube. (Figure 3-21-4) In cross section, the cracks tend to be bulbous with numerous lobes. (Figure 3-21-2 and Figure 3-21-5) The crack tips themselves may be somewhat blunted and are oxide filled and transgranular. (Figures 3-21-2, 3-21-3, and 3-21-5)

f) In sulfiding environments, cracks will have a similar appearance to non-sulfiding environments but will be filled with a sulfide scale.

3.21.6 Prevention/Mitigation

a) Rotating equipment.

1. Select an appropriate corrosion-resistant material.
2. Protect the component from corrosion using a coating, if applicable.
3. Modify the corrosive environment by using a corrosion inhibitor, if applicable
4. Minimize galvanic couple effects.

b) Deaerators.

1. Ensure the use of proper feedwater and condensate chemical control.

2. Minimize residual welding and fabrication stresses by using PWHT.

3. Minimize weld reinforcement stress concentrators by grinding weld contours smooth.

c) Cycling boilers.

1. Start up slowly to minimize differential expansion strains.

2. Ensure proper boiler water chemistry control at all times, including start-up.

3.21.7 Inspection and Monitoring

a) Rotating equipment.

1. VT as well as UT, PT, and MT techniques can be used for crack detection.

b) Deaerators.

1. Many of the cracks are very tight and difficult to detect. Inspection should focus on welds.

2. WFMT is the most widely used off-line detection method, especially where cracks are tightly filled with corrosion by-products. It may be necessary to remove internal fixtures to gain access to fillet and other welds for WFMT.

3. Angle beam UT (SWUT or PAUT) can be used to detect cracks from the OD; however, tightly filled cracks can be difficult to detect with UT.

4. ACFM or other eddy current techniques, including phase sensitive eddy current, can detect surface-breaking cracks on the ID surface where the cracks initiate.

5. PT can be used to detect cracks; however, it is highly dependent upon surface preparation, and tightly filled cracks may preclude detection. Long penetrant and developer dwell times may be needed.

6. Online cracking examinations are often limited due to process temperature and component configuration/geometry but may include advanced ultrasonic examinations techniques such as PAUT.

c) Cycling boilers.

1. The first sign of damage is usually a pinhole leak on the cold side of a waterwall tube at a buckstay attachment.

2. Highly stressed regions in the boiler where cracking can occur can be inspected using angle beam UT (SWUT or PAUT) or EMAT techniques.

3. Cracking may occur at the membranes in the highly stressed regions, particularly corners at buckstays.

3.21.8 Related Mechanisms

Mechanical fatigue (3.43), thermal fatigue (3.64), and boiler water and condensate corrosion (3.9).

3.21.9 References

1. *Steam—Its Generation and Use*, 40th Edition, Babcock and 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.

7. *ASM Handbook—Materials Characterization*, Volume 10, ASM International, Materials Park, OH.

8. API Technical Report 938-C, *Use of Duplex Stainless Steels in the Oil Refining Industry*, American Petroleum Institute, Washington, DC.

9. NACE SP0590, *Prevention, Detection, and Correction of Deaerator Cracking*, NACE International, Houston, TX.

Figure 3-21-1—Corrosion fatigue failure of a boiler tube.

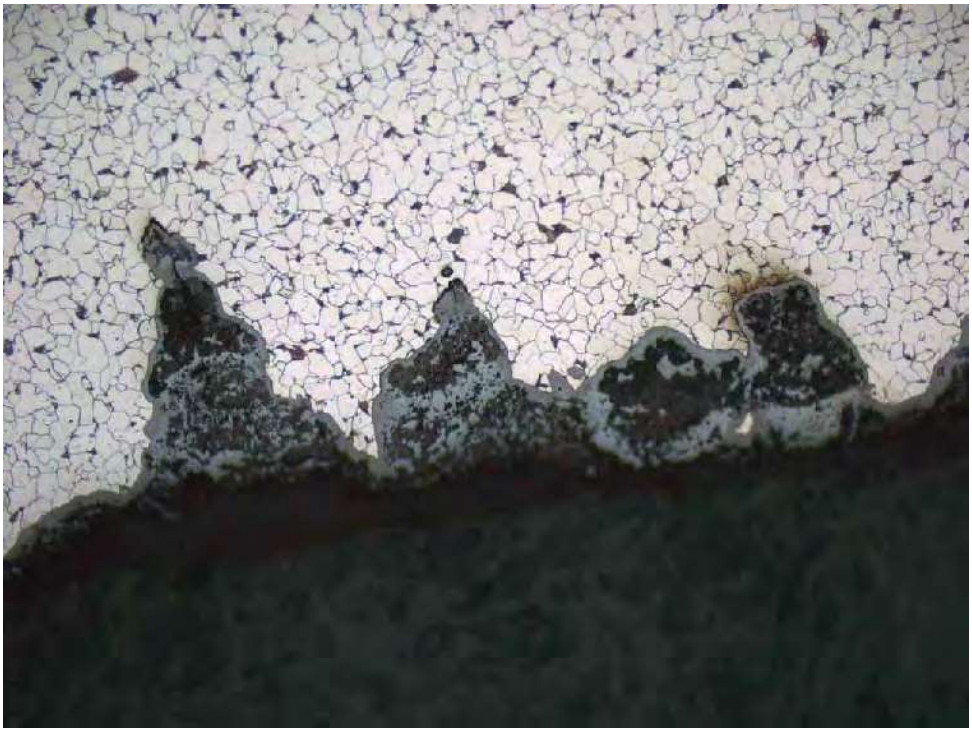


Figure 3-21-2—Metallographic mount of sample taken from failed boiler tube in Figure 3-20-1.

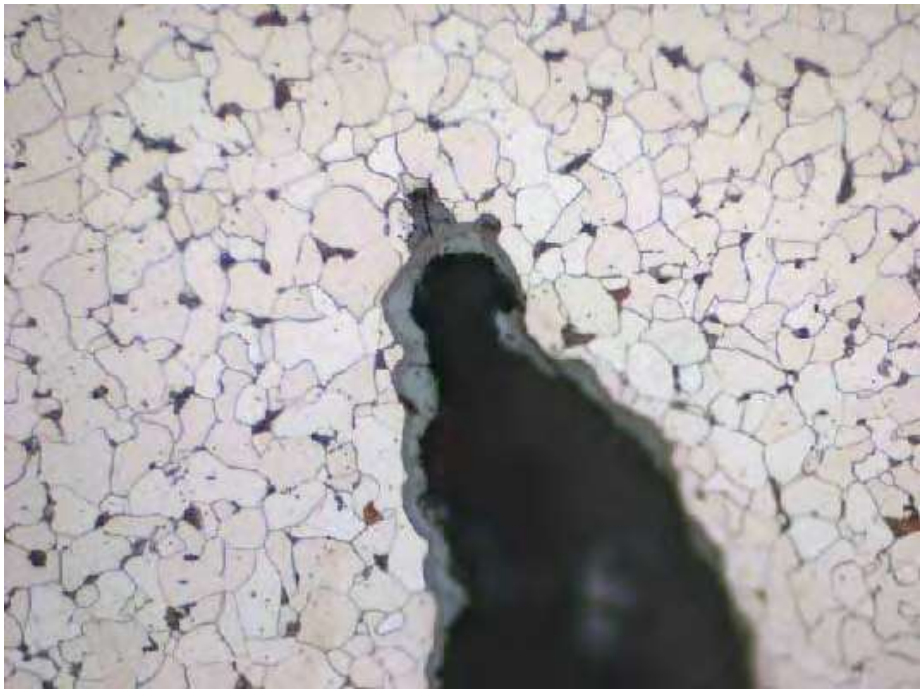


Figure 3-21-3—Higher-magnification view of sample shown in Figure 3-20-2.

Figure 3-21-4—Photograph of a carbon steel boiler tube cut in half lengthwise. Corrosion fatigue cracks initiated at the ID of the tube, opposite a buckstay attachment on the OD. (Magnification 1X.)

Figure 3-21-5—Photomicrograph showing the crack morphology that is rounded with multiple lobes and may branch to form "rabbit ears." (Magnification 25X, etched.)

3.22 Corrosion Under Insulation

3.22.1 Description of Damage

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

3.22.2 Affected Materials

Carbon steel, low-alloy steels, 300 series SS, 400 series SS, and duplex stainless steels.

3.22.3 Critical Factors

a) Temperature, duration of wetting, design of the insulation system, insulation type, and environment are critical factors.

   Corrosion rates increase with increasing metal temperature up to the point where the water evaporates quickly. While water boils or steams off above the boiling temperature, 212 °F (100 °C), it does not do so instantaneously. It takes some amount of time for water to boil off and wet insulation to dry out. During this time, the metal is corroding. The higher the temperature above the boiling point, the faster the water will evaporate and the insulation will dry out. However, with a high enough rate of wetting and replenishment of the water in the wet insulation, CUI can occur on equipment operating at virtually any temperature of practical concern in refining.

   1. In most situations, and as a practical matter, refiners generally focus their CUI management efforts on insulated carbon steel, low-alloy steel, and 400 series SS equipment operating between 10 °F (−12 °C) and 350 °F (175 °C).

   2. For 300 series SS, where Cl^- SCC is the concern, refiners generally focus on the temperature range of 140 °F (60 °C) to 350 °F (175 °C).

   3. For duplex stainless steel, where Cl^- SCC is the concern, refiners generally focus on the temperature range of 280 °F (140 °C) to 350 °F (175 °C).

b) The extent of CUI attack depends on the total amount of time the equipment remains wet from exposure to wet insulation. Therefore, while a higher operating temperature will result in a higher corrosion rate, the total amount of attack over a long period of time may occur at a lower temperature if the metal remains wet for significantly longer periods of time at the lower temperature. This is one of the reasons why CUI corrosion rates are difficult to predict.

c) Poor design or installation of insulation systems that allow water to become trapped will increase CUI.

d) Insulating materials that wick moisture can hold water and be more prone to causing extensive CUI.

e) Insulating materials that dry out slowly can be more prone to causing extensive CUI.

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

g) Equipment that operates below the water dew point tends to condense water on the metal surface, thus providing a wet environment and increasing the risk of corrosion.

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

i) Plants located in areas with high annual rainfall or warmer marine locations are more prone to CUI than plants located in cool and dry or warm and dry locations.

j) Environments that provide airborne contaminants such as chlorides (e.g. from marine environments or cooling tower drift) or SO_2 (e.g. from stack emissions) can accelerate corrosion.

3.22.4 Affected Units or Equipment

a) All insulated piping and equipment are susceptible to CUI under the conditions noted above, even piping and equipment where the insulation system appears to be in good condition and no visual signs of corrosion are present.

b) Examples of locations where CUI can occur are listed below.

1. CUI can be found on equipment with damaged insulation, insulation jacketing, vapor barriers, weatherproofing or mastic, or where caulking has hardened, separated, or is missing.

2. CUI can occur where water gains access at protrusions through the insulation or at insulation termination points such as flanges.

3. Piping components and locations that are particularly susceptible include dead-legs (vents, drains, and other similar items), pipe hangers and other supports, valves and fittings with irregular insulation surfaces, bolted-on pipe shoes, steam tracing tube or heat tracing wire penetrations, at the terminations of insulation at flanges or other piping components, at the termination of insulation in vertical pipe, and the first few feet of a horizontal pipe run adjacent to the bottom of a vertical run.

4. Piping or equipment with damaged and leaking steam tracing is susceptible.

5. Vibrating piping systems have a tendency to inflict damage to insulation jacketing providing a path for water ingress.

6. Insulation jacketing seams located on the top of horizontal piping or improperly lapped or sealed insulation jacketing can lead to CUI.

7. Locations where moisture or trapped water will naturally collect due to gravity drainage before evaporating such as low points in piping runs and insulation support rings on vertical columns, as well as improperly terminated fireproofing.

8. Equipment designed with insulation support rings welded directly to the vessel wall (i.e. with no standoff) can be susceptible, particularly around ladder and platform clips, lifting lugs, nozzles, and stiffener rings.

9. CUI can occur in carbon or low-alloy steel flanges, bolting, and other components under insulation in high-alloy piping systems.

10. Locations where insulation plugs have been removed to permit piping thickness measurements on insulated piping and equipment are a potential source of water ingress.

11. Where piping and equipment have been coated beneath the insulation, localized CUI can still occur where the coating has deteriorated or been damaged.

12. Equipment subjected to long-term or frequent water spray, e.g. from firefighting, fire equipment testing, or supplemental externally applied cooling, is highly susceptible to CUI.

13. 300 series SS equipment insulated with older calcium silicate insulation, which is known to contain high levels of chlorides, can suffer pitting, crevice corrosion, and Cl^- SCC.

3.22.5 Appearance or Morphology of Damage

a) Carbon steel and low-alloy steels are subject to corrosion having a rough, uneven, somewhat pitted appearance, usually covered with a loose, flaky, non-protective scale attached. The corrosion will be localized to wherever the metal has been kept wet by wet insulation. (Figure 3-22-1 to Figure 3-22-8)

b) In some cases, the corrosion can appear to be carbuncle-type pitting (usually found under failed coating).

c) 300 series SS are subject to SCC if chlorides are present. While the duplex stainless steels are less susceptible, SCC failures have occurred in duplex stainless steel due to CUI.

d) 300 series SS and duplex stainless steel are subject to pitting and crevice corrosion.

e) Telltale signs of CUI include insulation jacketing damage, bulges or staining of the insulation or jacketing, missing bands, coating damage, or vegetation growing out of the insulation. Bulges may indicate corrosion product buildup.

3.22.6 Prevention/Mitigation

a) Since most construction materials used in refining are susceptible to CUI damage, mitigation is best achieved by applying an appropriate coating to the equipment prior to insulating.

   1. High-quality, immersion-resistant nonmetallic coatings, properly applied to the surfaces to be insulated, can provide long-term protection.

   2. Flame-sprayed aluminum coatings have been used on carbon steels. The coating corrodes preferentially by galvanic action, thereby protecting the base metal.

b) Insulation, insulation jacketing, sealants, and vapor barriers should be properly maintained to prevent moisture ingress.

c) Thin aluminum foil wrapped on stainless steel piping and equipment beneath the insulation can provide an effective barrier, partly due to the galvanic effect of the aluminum in preventing Cl^- SCC in stainless steel.

d) Careful selection of insulating materials is important. Both water absorption properties and water retention characteristics are important and should be considered. Some insulating materials absorb little water but still trap water against the pipe or equipment for an extended time because water removal is slow. While closed-cell foam glass materials will hold less water and, therefore, might be less prone to causing CUI, studies show that an open cell structure provides a path for water vapor to escape faster, allowing the insulation to dry quicker. Faster drying time, corresponding to less metal wetting time, should help mitigate CUI.

   1. Types of open cell insulation that limit and delay water ingress have been developed.

   2. Water absorption and retention properties of insulation materials can be tested per EN 13472 or ASTM C1134.

e) Insulation with added corrosion inhibitor is available.

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

   1. Some manufacturers supply insulation certified to be low chloride. Thermal insulation materials can be tested per ASTM C871 to evaluate chloride content and/or ensure it satisfies a specified limit.

g) Insulation plugs removed for UT thickness measurements should be promptly replaced and sealed. Several types of removable plugs that permit inspection and identification of inspection points are commercially available.

h) Consider available alternatives in order to avoid the use of insulation where practical.

   1. Personnel protection from hot piping can be provided using metal-cage-type standoffs rather than insulation.

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

3.22.7 Inspection and Monitoring

a) An inspection plan for CUI should be a structured, systematic approach starting with prediction and analysis per the CUI planning information contained in API 510, API 570, and API 583. [API 583 was created specifically for CUI/CUF (corrosion under fireproofing) and should be referenced for a deeper understanding of inspection for these damage mechanisms.] The inspection plan should consider:

1. history of CUI leaks,
2. operating temperatures that may give rise to CUI,
3. type and age/condition of coating, and
4. type, age, and condition of the insulation material.

b) Additionally, an external VT of the equipment, looking for evidence of insulation system damage, mastic and/or sealant damage, signs of water penetration, rust in gravity drain areas on equipment and piping, and signs of process fluid leaks, will help prioritize the effort.

c) Although external insulation may appear to be in good condition, CUI damage may still be occurring in isolated areas not thought to be susceptible. The owner/user generally determines the extent of CUI inspection, including the extent of insulation removal for inspection, based on inspection and CUI history and other factors as described above.

1. An effective way to find all CUI damage is complete removal of insulation and inspection for damage using VT, UT, and/or a pit gage, as applicable, for determining remaining thickness, or PT to examine for external Cl^- SCC of austenitic stainless steels.
2. Inspection by RT (density and/or profile) or UT thickness inspection (e.g. using high-resolution pigging) can also provide a high level of CUI detection confidence, depending on the extent of inspection, i.e. the percent of potentially affected piping inspected.
3. In some instances, insulation “windowing” can be used to remove insulation in selected areas thought to be more susceptible to CUI damage than others and inspecting for damage using VT, UT, and/or a pit gage, as applicable, for determining remaining thickness, or PT to examine for external Cl^- SCC of austenitic stainless steels. However, this may be less effective than complete insulation removal.

d) Non-invasive, commercially available methods can be used to identify either wet insulation or CUI damage under the insulation without removing the insulation; however, these methods should not be expected to find 100 % of the damage. Each of these methods is discussed in API 583, including advantages and disadvantages of each. Most are screening techniques that may help identify where there is a higher probability of CUI damage and where insulation stripping may be needed to further assess and quantify the damage. These methods include, but may not be limited to:

1. GWT;
2. RT (including profile, density, flash, radiometric profiling, real-time, computed, and digital);
3. PEC;
4. neutron backscatter (for identifying wet insulation); and
5. infrared thermography imaging (for identifying wet insulation).

e) Common areas of higher CUI concern in process units are high-moisture areas such as those down-wind from cooling towers (the drift zone), near steam vents, under deluge systems, exposed to acid vapors, or near supplemental cooling with water spray.

3.22.8 Related Mechanisms

Atmospheric corrosion (3.8), oxidation (3.48), oxygenated water corrosion (3.49), concentration cell corrosion (3.19), and Cl^- SCC (3.17).

3.22.9 References

1. API Recommended Practice 583, Corrosion Under Insulation and Fireproofing, American Petroleum Institute, Washington, DC.

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

3. NACE Standard SP0198, *Control of Corrosion Under Thermal Insulation and Fireproofing Materials—A Systems Approach*, NACE International, Houston, TX.

4. W.I. Pollock and C.N. Steely, *Corrosion Under Wet Thermal Insulation*, NACE International, Houston, TX, 1990.

5. M.M. Chauviere et al., "Managing CUI in Aging Refinery Pressure Vessels," Paper No. 07566, *Corrosion/2007*, NACE International, Houston, TX.

6. API 510, *Pressure Vessel Inspection Code: In-Service Inspection, Rating, Repair, and Alteration*, American Petroleum Institute, Washington, DC.

7. API 570, *Piping Inspection Code: In-service Inspection, Repair, and Alteration of Piping Systems*, American Petroleum Institute, Washington, DC.

8. A.C. Haaland, "Designing against CUI—What Are the Implications of the Test Method Chosen?" Paper No. RISK16-8742, *Corrosion Risk Management Conference*, NACE International, Houston, TX, May 2016.

9. C. Zwaag and S.N. Rasmussen, "Cyclic CUI Testing of Insulation Materials," Paper No. 8877, *Corrosion/2017*, NACE International, Houston, TX.

10. EN 13472, *Thermal Insulating Products for Building Equipment and Industrial Installations—Determination of Short Term Water Absorption by Partial Immersion of Preformed Pipe Insulation,* Available as CSN EN 13472, DIN EN 13472, and BS 13472, European Committee for Standardization, Brussels, Belgium.

Figure 3-22-1—Piping tee in a 1000 psig ethylene line before insulation removal.

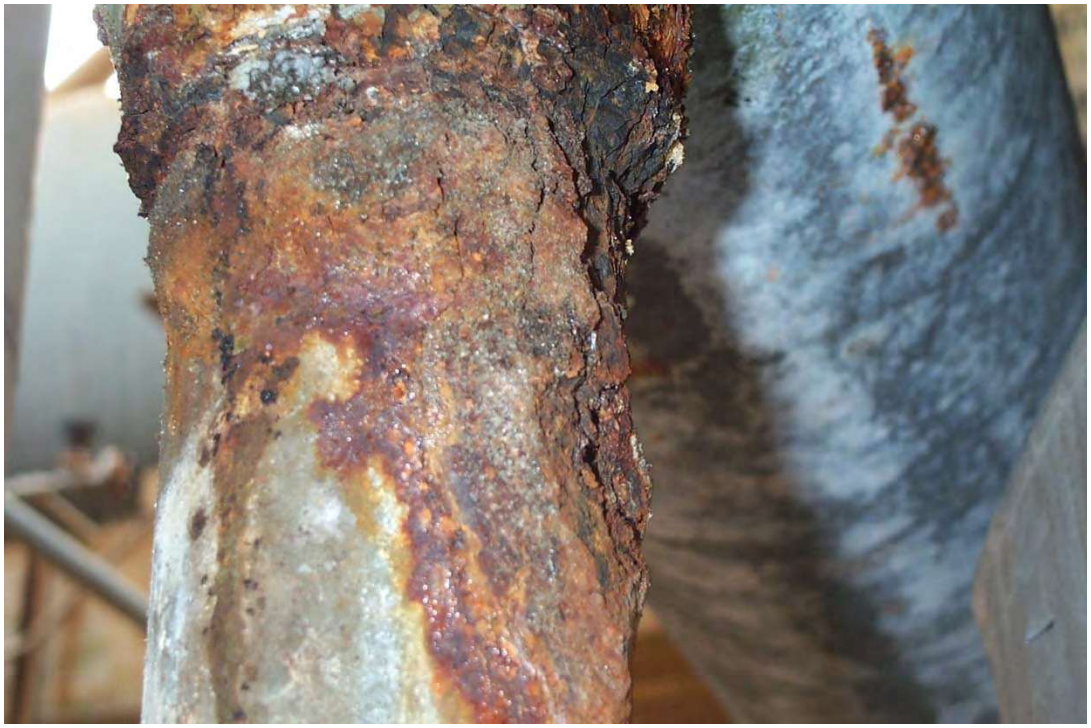


Figure 3-22-2—Close-up of the tee in Figure 3-21-1 after insulation removal.

Figure 3-22-3—CUI of a 30-in. carbon steel butadiene line showing highly localized corrosion that could only be found by stripping the entire line. Note the 0.25-in. (6.5-mm) diameter hole at arrow.

Figure 3-22-4—CUI of a nozzle on the bottom head of a pressure vessel.

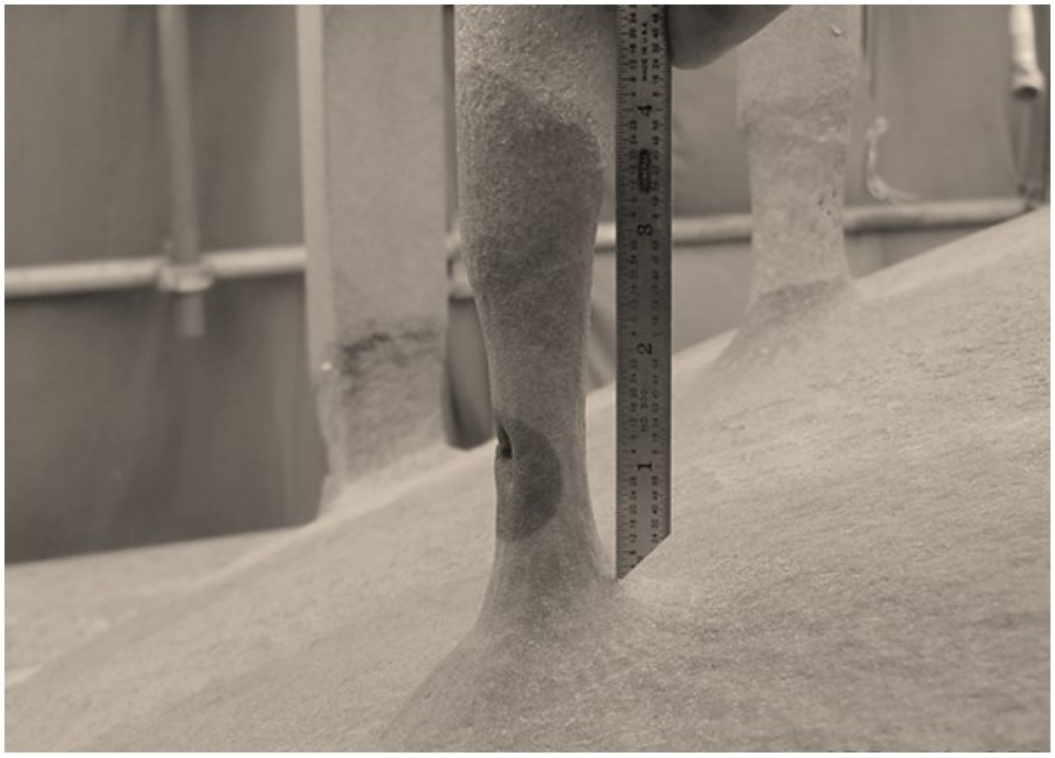


Figure 3-22-5—CUI of a nozzle on the top head of a pressure vessel.

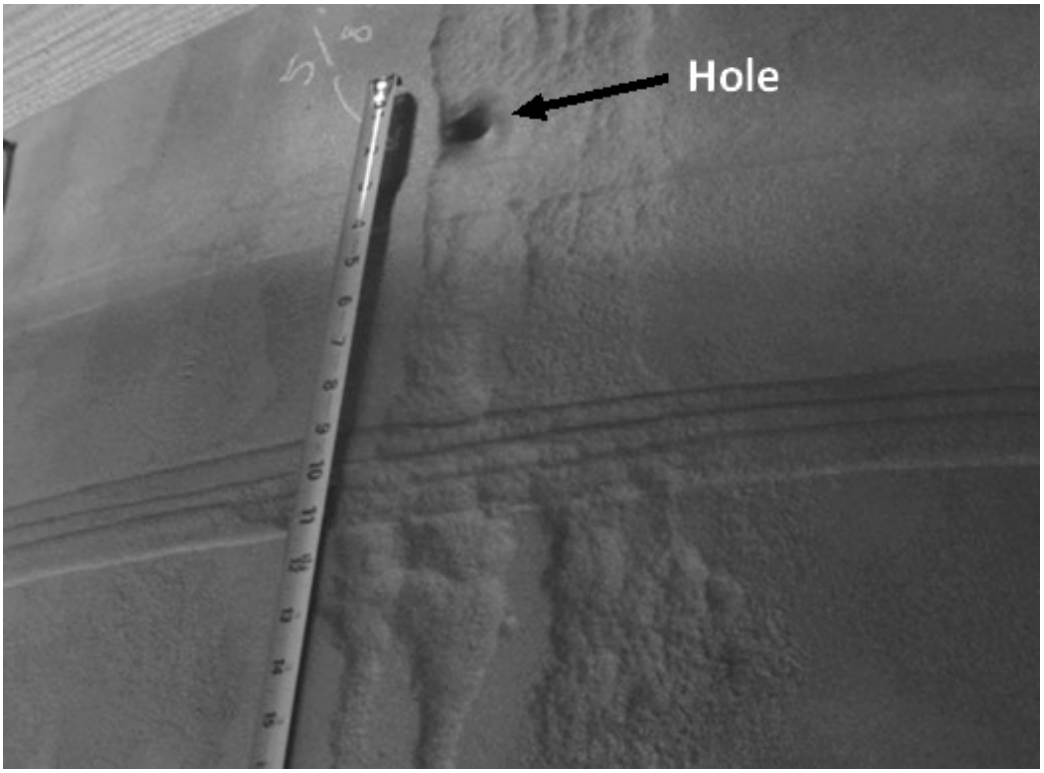


Figure 3-22-6—CUI of a vessel wall. Note the leak at the arrow.

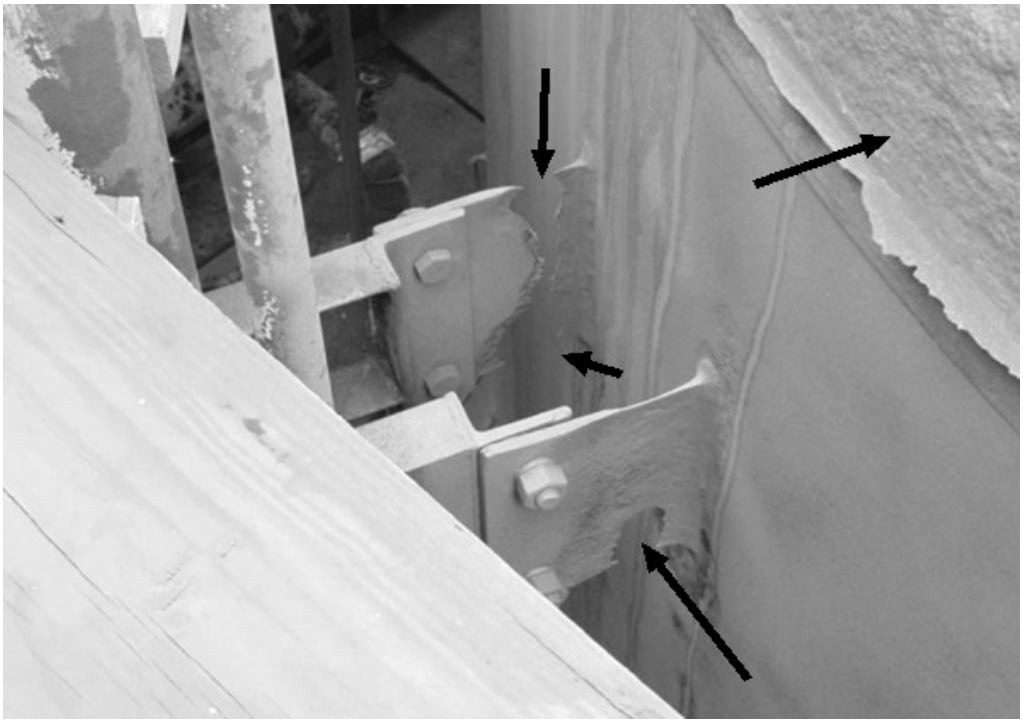


Figure 3-22-7—CUI at attachment supports and on the vessel head.

Figure 3-22-8—CUI of a carbon steel level bridle.

3.23 Creep and Stress Rupture

3.23.1 Description of Damage

a) At high temperatures [typically greater than half the absolute melting temperature in °R (°K)], metal components can continuously deform under load, even below their elastic yield stress. This time-dependent deformation of stressed components is known as creep.

b) Exposure to stress at high temperatures initially promotes void formation at grain boundary triple points, which with time grow to form fissures and, later, cracks.

c) As fissures and cracks coalesce, failure can occur, although the gross deformation associated with tensile overloading is not observed.

3.23.2 Affected Materials

All metals and alloys.

3.23.3 Critical Factors

a) The rate of creep deformation (creep rate or strain rate) is a function of the material, applied stress, and temperature.

   1. Creep rate is very sensitive to relatively small changes in temperature or stress. Generally, a temperature increase of about 25 °F (15 °C) or a 15 % increase in stress can cut the remaining life in half, or worse, depending on the alloy.

b) Table 3-23-1 lists threshold temperatures for different metals above which creep damage is a concern. If the metal temperature exceeds these values, creep deformation and creep cracking can eventually occur.

c) The creep life of metal components becomes extremely long at temperatures below their threshold in Table 3-23-1, even at the high stresses near a crack tip.

d) Creep deformation is the result of relative movement between individual (microscopic size) grains or other discontinuities within the metal. As creep progresses and cracks develop and grow from microscopic size to macroscopic size, the cracks eventually grow through the wall resulting in failure, at which point they are clearly visible.

   1. Because a coarse-grained material has less grain boundary surface area than a fine-grained material, a material heat treated to have a coarse-grained structure will generally have better creep strength than the same material with a fine-grained structure.

e) Creep cracking, once initiated, can progress rapidly.

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

g) The appearance of creep cracking with little or no apparent deformation usually indicates that the material has low creep ductility. Low creep ductility is:

   1. more pronounced in higher tensile strength materials and welds,

   2. more prevalent at lower temperatures in the creep range or with low stresses at the upper temperatures in the creep range,

   3. more likely in a coarse-grained material than in a fine-grained material,

   4. not evidenced by a deterioration of ambient temperature properties, and

   5. promoted by certain carbide types in some Cr-Mo steels.

3.23.4 Affected Units or Equipment

a) Creep damage is found in high-temperature equipment operating in the creep temperature range. Heater tubes in fired heaters, as well as tube supports, hangers, and other furnace internals, as well as high-pressure steam tubes in boilers, can be susceptible to creep.

b) Hot-wall catalytic reforming reactors, reactor piping, furnace tubes, hydrogen-reforming furnace tubes, hot-wall FCC reactors, and FCC main fractionator and regenerator internals all operate in or near the creep temperature range.

c) Low creep ductility failures have occurred in weld HAZs at nozzles and other high-stress areas in 1¼Cr-½Mo catalytic reformer reactors. Cracking has also been found at long seam welds in some high-temperature 1¼Cr-½Mo piping and reactors in catalytic reformers, primarily due to “peaking” of the long-seam welds.

d) Welds joining dissimilar materials (e.g. ferritic to austenitic welds) may suffer creep-related damage at high temperatures due to differential thermal expansion stresses.

3.23.5 Appearance or Morphology of Damage

a) The initial stages of creep damage can only be identified by scanning electron microscope (SEM) metallography. Creep voids typically show up at the grain boundaries. At later stages, they grow into microfissures and then cracks. When the fissures run the entire length of a grain boundary, they can be seen by standard optical microscope metallography, although they will not necessarily be easy to find.

b) At temperatures well above the threshold limit, noticeable deformation may be observed. For example, heater tubes may suffer long-term creep damage and exhibit significant, measurable bulging before rupture occurs. The amount of deformation before fracture is highly dependent on the material and the combination of temperature and stress level. (Figure 3-23-1 to Figure 3-23-3)

c) In vessels and piping, creep cracking can occur where high metal temperatures and stress concentrations occur together, such as near major structural discontinuities including pipe tee joints and vessel nozzles, as well as at weld flaws.

3.23.6 Prevention/Mitigation

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

b) Low creep ductility can be minimized by the careful selection and specification of materials. See SRC (3.54).

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

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

2. Fired Heater Tubes—Alloys with improved creep resistance may be required for longer life. Heaters should be designed and operated to minimize hot spots and localized overheating, e.g. due to flame impingement or improper burner operation. (Figure 3-23-3) Minimizing process-side fouling and deposits and fire-side deposits and scaling, both of which can necessitate overfiring to maintain process temperatures, can maximize tube life.

3. Remaining life of heater tubes can be assessed in accordance with API 579-1/ASME FFS-1.

4. Retirement criteria based on diametric growth and loss of wall thickness are highly dependent on the tube material and the specific operating conditions. Different retirement strategies may be needed for different situations.

3.23.7 Inspection and Monitoring

a) Creep deformation and the associated microvoid formation, fissuring, and dimensional change are not effectively found by any one inspection technique. A combination of proper NDE techniques (surface and volumetric), dimensional measurements, and field metallographic replication (FMR) are often needed. Destructive sampling and metallographic examination are generally used to confirm damage.

1. Conventional NDT methods, e.g. WFMT, VT, PT, or UT techniques, are not able to detect creep damage prior to the formation of a creep crack.

2. FMR is typically used where evidence has been found through other inspection methods.

NOTE FMR performed on the surface of a component will not show subsurface damage and will miss internal creep fissuring.

b) For pressure vessels, inspection is generally focused on welds of Cr-Mo alloys operating in the creep range. The choice of NDE methods may depend on the severity of any apparent damage. On the viewable surface, VT is generally performed, followed up with PT or WFMT. For subsurface examination for cracking or gross fissuring, angle beam UT (SWUT or PAUT) or other high-resolution NDE methods, such as TOFD, can also be employed, although the early stages of creep damage are very difficult to detect.

c) Fired heater tubes are typically inspected for evidence of overheating, bulging, corrosion, and erosion as follows.

1. Tubes can be VT examined for bulging, blistering, cracking, sagging, bowing, or rubbing wear. VT will not detect internal creep damage but is used to identify areas where further NDE may be needed.

2. UT wall thickness measurements of selected heater tubes can be made where wall losses are most likely to occur. UT thickness measurements will not detect creep damage but are used for creep examination to identify areas where further NDE may be needed.

3. Tubes can be examined for evidence of diametric growth due to creep with a strap or go/no go gauge. Dimensional inspection will not detect internal creep damage but will detect large, apparent creep deformation and also identify areas where further NDE may be needed.

4. In-line inspection (smart pigging) of heater tubes will provide a more complete assessment of remaining wall thickness and diameter growth. However, it is unlikely to detect internal creep damage, and further NDE may be needed.

5. Automated inspection devices (crawlers) are commercially available for inspecting hydrogen reformer heater tubes. The selection of such equipment for inspection, as well as analysis and interpretation of results, involves careful evaluation.

3.23.8 Related Mechanisms

Short-term overheating—stress rupture (3.55), SRC (3.54), and dissimilar metal weld (DMW) cracking (3.26).

3.23.9 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.

Table 3-23-1—Threshold Temperatures for Creep (Reference 1)

Material	Temperature Limit
Carbon steel [UTS > 414 MPa (60 ksi)]	650 °F (345 °C)
Carbon steel [UTS > 414 MPa (60 ksi)]	700 °F (370 °C)
Carbon steel—Graphitized	700 °F (370 °C)
C-½Mo	750 °F (400 °C)
1¼Cr-½Mo—Normalized and tempered	800 °F (425 °C)
1¼Cr-½Mo—Annealed	800 °F (425 °C)
2¼Cr-1Mo—Normalized and tempered	800 °F (425 °C)
2¼Cr-1Mo—Annealed	800 °F (425 °C)
2¼Cr-1Mo—Quenched and tempered	800 °F (425 °C)
2¼Cr-1Mo-V	825 °F (440 °C)
3Cr-1Mo-V	825 °F (440 °C)
5Cr-½Mo	800 °F (425 °C)
7Cr-½Mo	800 °F (425 °C)
9Cr-1Mo	800 °F (425 °C)
9Cr-1Mo-V	850 °F (455 °C)
12 Cr	900 °F (480 °C)
AISI Type 304 and 304H	950 °F (510 °C)
AISI Type 316 and 316H	1000 °F (540 °C)
AISI Type 321	1000 °F (540 °C)
AISI Type 321H	1000 °F (540 °C)
AISI Type 347	1000 °F (540 °C)
AISI Type 347H	1000 °F (540 °C)
Alloy 800	1050 °F (565 °C)
Alloy 800H	1050 °F (565 °C)
Alloy 800HT	1050 °F (565 °C)
HK-40	1200 °F (650 °C)

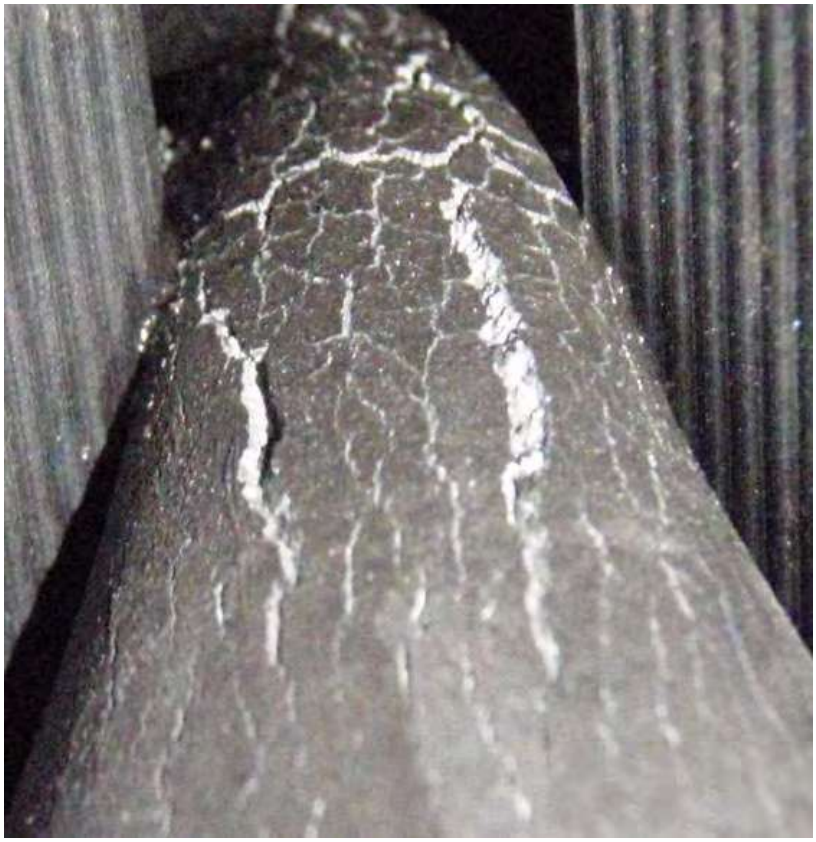
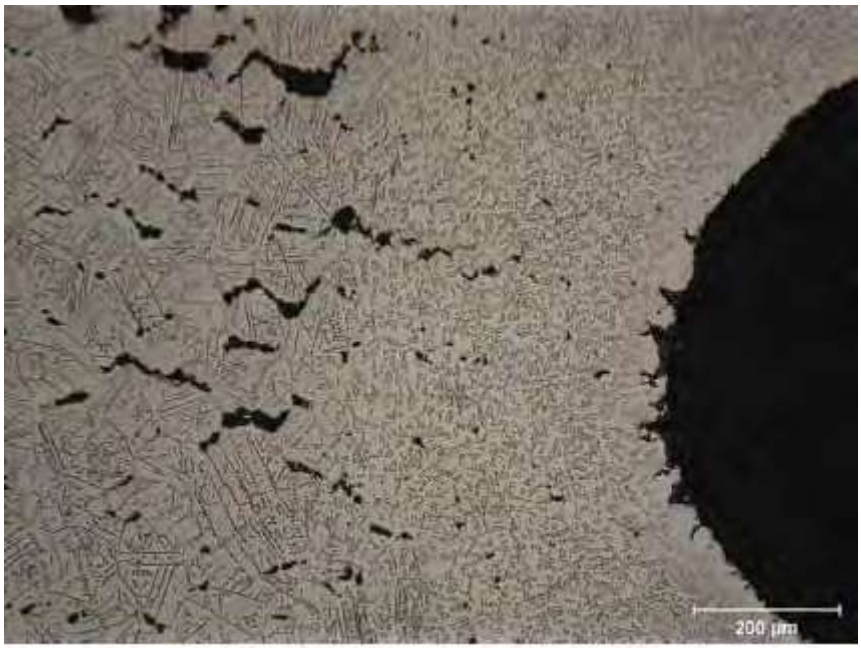


Figure 3-23-1—A pinched Alloy 800H pigtail with opened-up creep fissures on the surface.

Figure 3-23-2—Creep rupture of an HK40 heater tube.

(a)



(b)

Figure 3-23-3—Creep failure of Type 310 SS heater tube guide bolt after approximately 7 years of service at 1400 °F (760 °C). (a) Cross section at 10X magnification, as-polished. (b) Voids and intergranular separation characteristic of long-term creep (magnification 100X, etched).

3.24 Dealloying [See Graphitic Corrosion (3.33) for Dealloying of Cast Iron]

3.24.1 Description of Damage

a) Dealloying is the result of what appears to be a selective corrosion mechanism in which one or more constituents of an alloy are preferentially attacked, leaving a lower-density (dealloyed), often porous structure.

b) Component failure may occur suddenly and unexpectedly because mechanical properties of the dealloyed material are significantly degraded.

3.24.2 Affected Materials

Primarily copper alloys (brasses and bronzes and Cu-Ni alloys) as well as Alloy 400.

3.24.3 Critical Factors

a) Factors that influence dealloying include the composition of the alloy and the exposure conditions including temperature, presence or increase levels of oxygen or aeration, pH, and exposure time.

b) Dealloying occurs with several different alloys but is usually limited to very specific alloy-environment combinations.

c) Exact conditions under which dealloying occurs are often hard to define and damage may occur progressively over many years in service.

d) Stagnant or low-flow conditions can promote dealloying.

e) Common examples of where dealloying has been found to occur are listed in Table 3-24-1.

3.24.4 Affected Units or Equipment

a) Copper alloys in cooling water applications, including tubes and tubesheets, can be susceptible to dealloying in some brackish and seawater applications. Dealloying can also occur in some freshwater or domestic water systems.

b) In BFW piping systems and after-boiler systems, bronze pumps, Alloy 400 strainers, brass pressure gage fittings, steam turbine surface condenser tubes, and the like may suffer dealloying.

c) Alloy 400 exposed to HF acid in HF alkylation plants can be susceptible to denickelification, particularly above 300 °F (50 °C) or if oxygen is present.

3.24.5 Appearance or Morphology of Damage

a) There is often a significant color change, with the affected area becoming the color representative of the remaining material. The surface of the affected area can also have a dull or deeply etched (corroded) appearance as one element is removed from the alloy. However, depending on the alloy, the outward appearance of the affected material may not be noticeable upon VT, even where the full wall thickness is degraded.

b) Attack may be uniform through the cross section (layer-type) (Figure 3-24-1), or it can be localized (plug-type) (Figure 3-24-2).

c) In some cases, the original material is completely dealloyed, yet the component exhibits virtually no dimensional or other visible changes.

d) The porous, dealloyed material is often brittle and weak and may be easily broken off, even by hand. Thru-wall dealloying can result in fracture of the component or holes.

3.24.6 Prevention/Mitigation

a) It is often difficult to predict whether conditions will be conducive to dealloying in a particular environment or service, so one must be cognizant of the susceptibility of certain alloys and the possible resulting consequences.

b) Select “inhibited” versions of copper alloys. In some cases, resistance to dealloying can be improved by the addition of certain alloying elements, so that an alloy with only a slightly modified composition may be resistant. For example, admiralty brass is inhibited by the addition of a very small amount of phosphorous, antimony, or arsenic, while tin inhibits dealloying of other copper alloys. It is now typical for brass and bronze components used in refining applications to be sold only with the inhibited chemistry

c) Dealuminification of aluminum-bronze can be prevented by heat treatment to produce an α and β microstructure.

d) Use alternative materials that are not susceptible to dealloying in the environment(s) to which the they will be exposed.

e) Continued degradation of a dealloyed component can only be prevented by altering the exposure conditions or replacing it with a resistant material.

f) Depending on the alloy-environment combination, cathodic protection or barrier coatings may be effective.

g) Prevent the entry of oxygen into HF acid alkylation units.

3.24.7 Inspection and Monitoring

a) Many alloys change color in the affected area; however, scale removal may be required to determine the depth of attack.

b) Dealloying in brasses is visually evident by a reddish, copper color instead of the yellow brass color.

c) Metallographic examination may be required to confirm the extent of damage.

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

e) Acoustic techniques (loss of “metallic ring”) and ultrasonic attenuation are applicable, but UT thickness measurements are not.

f) FFS analysis of dealloyed components should consider that the dealloyed portion may be brittle and contribute little or no mechanical strength or load-bearing capability.

g) Electromagnetic techniques may be used to screen for dealloying. It is critical that the appropriate calibration standards be used. ECT can screen for dealloying in brass.

3.24.8 Related Mechanisms

Graphitic corrosion of cast irons (3.33). Dealloying is often referred to by the element removed, as in dezincification, destannification (tin), denickelification, and dealuminification. Dealloying has also been referred to as selective leaching.

3.24.9 References

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

2. A. Cohen, "Copper and Copper-base Alloys," *Process Industries Corrosion—The Theory and Practice*, NACE International, Houston, TX, 1986, pp. 479–501.

3. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991, pp. 259–263.

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

Table 3-24-1—Combinations of Alloys and Environment Subject to Dealloying (Reference 1)

Alloy	Environment	Element Removed
Brasses (>15 % Zn) *	Many waters, especially stagnant conditions	Zinc (dezincification)
Aluminum bronze (primarily with > 8 % Al)	HF acid, acids w/chloride ions, seawater	Aluminum (dealuminification)
Silicon bronzes	High-temperature steam and acidic species	Silicon (desiliconification)
Tin bronzes	Hot brine or steam	Tin (destannification)
Copper nickels (70 to 30)	High heat flux and low water velocity	Nickel (denickelification)
Monel	Hydrofluoric and other acids	Nickel (denickelification)
* The extent of dezincification increases with increasing zinc content.		

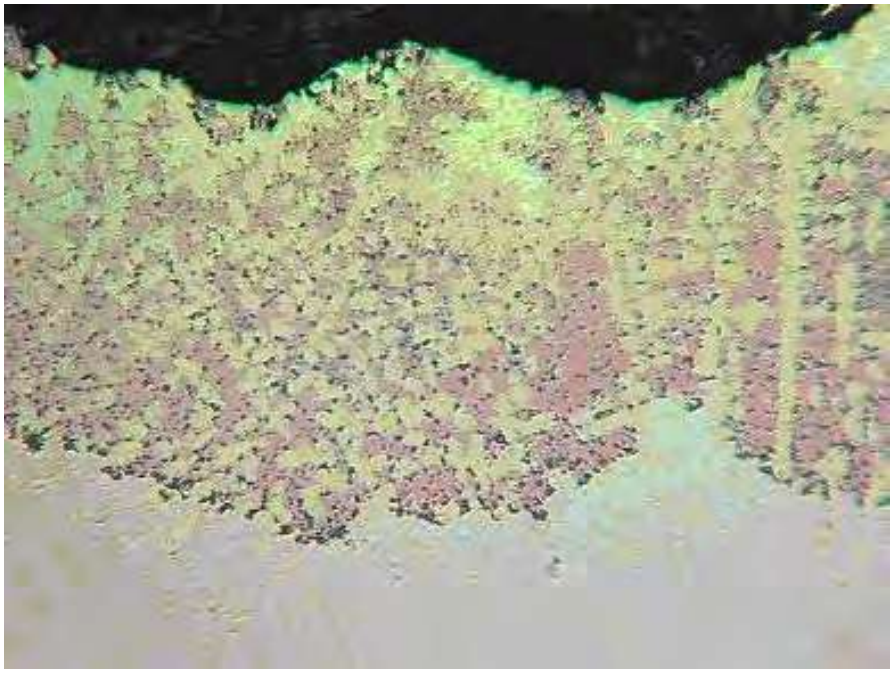


Figure 3-24-1—Cross section of a silicon-brass alloy, C87500, pump impeller from stagnant fire-water service. Layer-type dezincification depleted the zinc and left this porous red color of the copper. Magnification 50X.

Figure 3-24-2—A zone of denickelification in an Alloy 400 valve plug (at the port), due to oxygen contamination in hot hydrofluoric acid.

3.25 Decarburization

3.25.1 Description of Damage

A condition where a steel loses strength due to the removal of carbon and carbides leaving only an iron matrix. Decarburization occurs during exposure to high temperatures, during heat treatment, from exposure to fires, or from high-temperature service in a gaseous environment. Loss in room-temperature tensile strength and creep strength may potentially occur.

3.25.2 Affected Materials

Carbon steels and low-alloy steels.

3.25.3 Critical Factors

a) Time, temperature, and carbon activity of the process stream are the critical factors.

b) The material must be exposed to a gas phase that has a low carbon activity so that carbon in the steel will diffuse to the surface to react with gas phase constituents.

c) The extent and depth of decarburization is a function of the temperature and exposure time.

d) Shallow decarburization can slightly decrease the strength of the material but typically has no detrimental effect on the overall performance of the component. However, it is indicative that the steel may have been overheated and suggests other effects may be present [e.g. decarburization associated with high-temperature hydrogen attack (HTHA) in hydrogen services].

3.25.4 Affected Units or Equipment

a) Decarburization can occur in almost any equipment that has been heat treated, exposed to elevated service temperatures, or exposed to a fire.

b) Piping and equipment in hot hydrogen service in hydroprocessing units or catalytic reforming units, as well as most fired heater tubes, can be decarburized in service. Pressure vessel components that are hot formed during fabrication can be affected.

3.25.5 Appearance or Morphology of Damage

a) Damage can be verified by metallography.

b) Damage occurs on the surface exposed to the gas environment but in extreme cases may be through the wall.

c) The decarburized layer will be free of carbide phases. Carbon steel will become pure iron. (Figure 3-25-1 and Figure 3-25-2)

3.25.6 Prevention/Mitigation

a) Decarburization can be controlled by controlling the chemistry of the gas phase and alloy selection.

b) Alloy steels with chromium and molybdenum form more stable carbides and are more resistant to decarburization.

c) Steels operating in high-temperature hydrogen environments should be selected in accordance with API RP 941.

3.25.7 Inspection and Monitoring

a) VT is ineffective for detecting decarburization.

b) Inspection for decarburization in the initial stages of attack is difficult (and generally unnecessary).

c) FMR can be applied if the process-side surfaces are accessible, but it is often inconclusive.

d) Decarburization results in a softening that can be confirmed by hardness testing if the depth of decarburization is sufficient to enable accurate hardness testing results. This should be considered a screening tool. If the surface hardness falls below a set limit, which would differ between materials, then further testing (e.g. sampling and metallography) would likely be needed.

e) Decarburization can only be determined accurately by a chemical or physical test, which typically requires destructive sampling. Sampling location, condition, and preparation are critical.

3.25.8 Related Mechanisms

HTHA (3.36).

3.25.9 References

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

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

3. API Recommended Practice 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*, American Petroleum Institute, Washington, DC.

4. G. Vander Voort, “Understanding and Measuring Decarburization,” *Advanced Materials & Processes*, February 2015, pp. 22–27.

5. G. Vander Voort, “Decarburization,” Vac Aero International, http://vacaero.com/information-resources/metallography-with-george-vander-voort/1342-decarburization.html.

6. L. Garverick, *Corrosion in the Petrochemical Industry*, Second Edition, pp. 29, 150, 154, 227, 321, and 387, ASM International, Materials Park, OH.

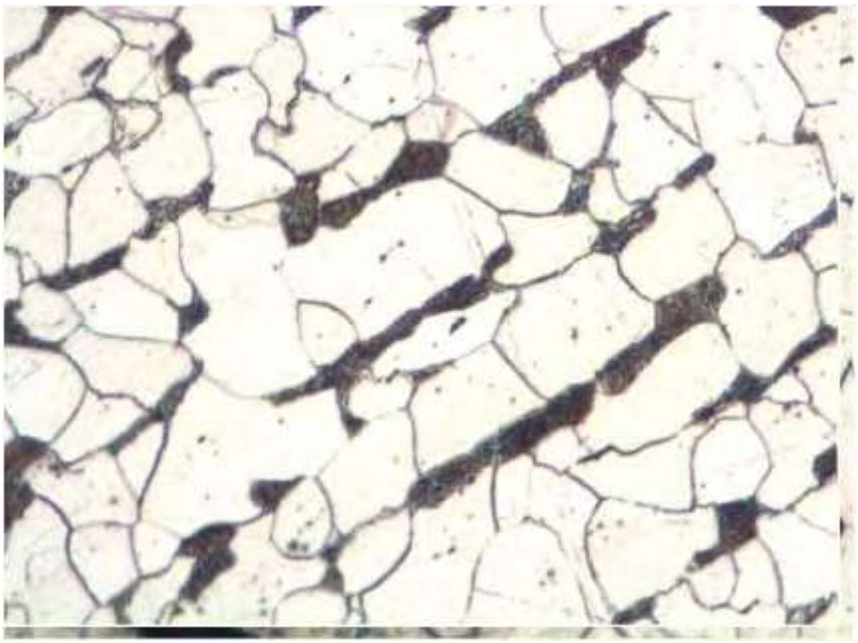


Figure 3-25-1—Typical low-carbon-steel microstructure showing ferrite phase (light grains) and pearlite (dark layered constituent).

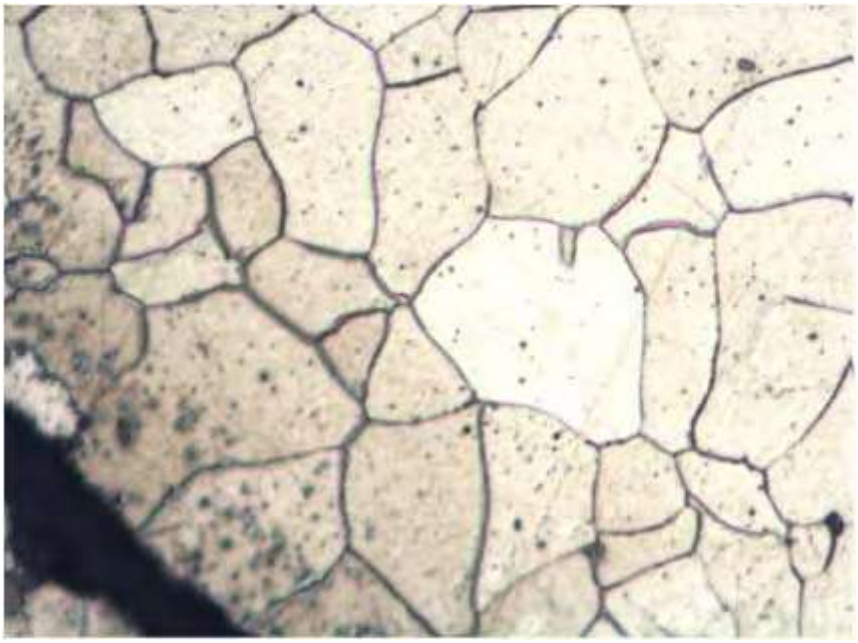


Figure 3-25-2—Microstructure illustrating a decarburized low carbon steel where the strength-providing pearlite constituent has been decomposed as the result of the removal of carbon atoms by diffusion to the surface.

3.26 Dissimilar Metal Weld Cracking

3.26.1 Description of Damage

There are four situations that can result in the cracking of DMWs. In one, operation at elevated temperature, about 500 °F (260 °C) or higher, results in high differential thermal expansion stresses at the weld that lead to creep cracking or creep-fatigue cracking. In the second, operation in a wet H_2S or similarly severe hydrogen charging environment leads to cracking in the hard, dissimilar metal mixed zone in the weld created when the two metals are melted together. The third, with some similarities to the second, occurs on the carbon steel side in welds between carbon steel and Alloy 400 in hydrofluoric acid service due to HE and/or fluoride wedging. In the fourth situation, DMW joints in (and weld overlay on) equipment in high-temperature hydrogen service can suffer disbonding between the two metals. This is commonly referred to as hydrogen disbonding. All four cases typically involve carbon steel or low-alloy steel welded to an austenitic (300 series) stainless steel or a nickel-based alloy.

3.26.2 Affected Materials

The most common are ferritic materials such as carbon steel and low-alloy steels welded to austenitic stainless steels. In HF acid service, it involves carbon steel welded to Alloy 400. Cracking due to high differential thermal expansion stress can occur in any material combination having widely differing thermal expansion coefficients.

3.26.3 Critical Factors

a) Thermal expansion related cracking. (See Figure 3-26-1 and Figure 3-26-2.)

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

2. Cracking can occur because the coefficients of thermal expansion of ferritic materials (e.g. steels) and austenitic materials (e.g. 300 series SS and nickel-based alloys) differ by about 25 % to 30 %. (See Table 3-26-1.) At high operating temperatures, the differences in thermal expansion lead to high shear stresses concentrated at the fusion line, primarily in the ferritic-side HAZ. The higher the operating temperature, the greater the stress created by the differential thermal expansion between the metals. Ferritic/austenitic joints can generate significant thermal expansion/thermal fatigue stresses at temperatures greater than 500 °F (260 °C). Cracking is most common at service temperatures greater than 800 °F (425 °C).

3. Thermal cycling aggravates the problem. Stresses during start-up and shutdown can be significant.

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

5. The problem is aggravated by the diffusion of carbon out of the HAZ of the ferritic material and into the austenitic weld metal where it is more soluble. The loss of carbon creates a “soft zone” with reduced creep strength in the ferritic material HAZ, thereby increasing the cracking probability. (Figure 3-26-3) The temperature at which carbon diffusion becomes a concern is above 800 °F (425 °C) for carbon steel and above 950 °F (510 °C) for low-alloy steels.

6. Poor geometry of the weld, excessive undercut, and other stress intensification factors will promote crack formation.

7. In environments that promote liquid ash corrosion, weld cracking problems may be accelerated by stress-assisted corrosion. The ferritic HAZ will preferentially corrode due to the large thermal strain. The results are long, narrow, oxide wedges that parallel the fusion line of the weld. (Figure 3-26-10)

b) Hard mixed metal zone related cracking.

1. DMWs between ferritic and austenitic materials that are made with a 300 series SS or nickel-based filler metal result in a narrow region (mixed zone) of high hardness along the fusion line on the ferritic steel side. These high-hardness zones render the material susceptible to HE types of environmental cracking such as SSC or hydrogen stress cracking. (Figure 3-26-4 and Figure 3-26-5) PWHT of the weldment will not prevent environmental cracking if the weld is exposed to wet H_2S conditions.

2. Poor geometry of the weld, excessive undercut, and other stress intensification factors will promote crack formation.

c) Cracking in HF acid.

1. Locating a CS to Alloy 400 weld in locations exposed to hydrofluoric acid (anhydrous HF, water containing HF, and dilute HF) creates a corrosive galvanic cell. The corrosion reaction produces hydrogen on the metal surface, which can then diffuse into the weldment. The problem is enhanced by high hardness in the coarse-grained HAZ of the carbon steel.

d) Hydrogen disbanding.

1. Joint design is critical for DMWs in high-temperature service in hydrogen environments. The weld joints must be carefully designed and inspected to prevent hydrogen disbonding. (Figure 3-26-6 to Figure 3-26-9)

3.26.4 Affected Units or Equipment

a) DMWs are utilized in special applications in refineries and other process plants. Examples of DMWs include the following.

1. Welds used to join clad pipe in locations such as transitions in hydroprocessing reactor outlet piping from overlaid low-alloy Cr-Mo nozzles or piping to solid 300 series SS pipe.

2. Hydroprocessing exchanger inlet and outlet piping.

3. Alloy transitions inside fired heaters (e.g. 9Cr to 317L in a crude furnace).

4. Hydrogen reformer furnace 1.25Cr inlet pigtails to Alloy 800 sockolets or weldolets on hydrogen reformer tubes.

5. Hydrogen reformer furnace Alloy 800 outlet cones to CS or 1.25Cr refractory lined transfer lines.

6. Welds joining clad pipe sections to themselves or to unclad carbon or low-alloy steel pipe (e.g. Alloy C276 clad CS piping in crude unit overhead system).

7. Nickel-based alloy welds joining socket weld valves in 5 and 9 Cr piping systems.

8. Carbon steel to Alloy 400 welds in HF alkylation units.

9. 300 series SS weld overlay in numerous refinery reactors and pressure vessels.

10. Similar DMWs have been used in FCC unit reactors and regenerator vessels and in coker units.

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

3.26.5 Appearance or Morphology of Damage

a) In most cases, differential thermal expansion cracks form at the toe of the weld in the HAZ of the ferritic material. (Figure 3-26-4 to Figure 3-26-10) Welds joining pipes or tubes are the most common problem area, but support lugs or attachments of cast or wrought 300 series SS to 400 series SS are also affected.

b) Hard mixed zone cracking occurs along the fusion line, through the mixed zone identifiable by metallographic examination.

c) Carbon steel to Alloy 400 weld damage in HF will be characterized by localized corrosion of the carbon steel HAZ area and hydrogen stress cracking along the fusion line or coarse-grained portion of the HAZ. (Figure 3-26-11 and Figure 3-26-12)

d) Hydrogen disbonding cracks form at the interface between the austenitic weld metal and the ferritic base metal.

3.26.6 Prevention/Mitigation

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

b) For high-temperature installations, consider installing a pup piece that has an intermediate thermal expansion coefficient between the two materials to be joined.

c) Use of a shallower weld prep bevel or a compound angle bevel increases the effective weld length and alters the stress field, which may promote longer life.

d) If 300 series SS welding electrodes are used, the DMW should be placed in a low-temperature region.

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

f) For high-temperature service, consider buttering the ferritic side of the joint with the stainless steel or nickel-based filler metal and perform PWHT prior to completing the DMW. PWHT will reduce residual stress at the ferritic-austenitic interface and thereby reduce the likelihood of high-temperature DMW cracking.

g) On buttered joints, the thickness of the weld metal should be a minimum of 0.25 in. (6 mm) after the bevel is machined, in order to avoid creating an HAZ in the base metal beneath the butter layer when the attachment weld is made.

h) Avoid using DMWs for socket welds or pressure-retaining fillet welds at temperatures above 250 °F.

i) Avoid using DMWs in wet H_2S services. Where unavoidable, specially designed weld configurations may be needed to avoid the potentially hard HAZ from contacting the environment or to avoid the formation of a thru-wall hard HAZ, e.g. by alloy-overlaying the base metal for some distance beyond the alloy weld joint.

j) Avoid using DMWs in HF acid service. Where necessary, locate the carbon steel to Alloy 400 transition where the exposure to free HF is minimal. In piping, use flanged connections. In lined columns, locate the DMW in an acid-free zone. Where exposure to HF cannot be avoided, take precautions to avoid high-hardness HAZs in carbon steel, particularly in older, pre-1980 steels. See NACE SP0472.

3.26.7 Inspection and Monitoring

Inspection of complex, multi-material welded joints may require consulting a subject matter expert and is beyond

the scope of this document.

a) The following techniques (alone or in combination) should be considered for NDE of dissimilar welds during fabrication:

   1. PT [prep, root pass, hot pass, cap pass, final inspection, and butter layer after PWHT (if applicable)];
   2. Angle beam UT* (SWUT or PAUT) on butt welds;
   3. UT on butter layer after PWHT (if applicable) to check bonding;
   4. RT;
   5. WFMT (magnetic materials only); and/or
   6. positive materials identification (PMI) can be used to confirm the chemical compositions of the different materials involved.

b) In fired heater tubes, RT and UT* (shear wave or phased array) can be used.

c) For inspection of cladding associated with dissimilar welds, UT* [straight beam or angle beam (SWUT or PAUT)] or ECT can be used.

d) For inspection for creep damage due to DMWs, there is no reliable NDE method to detect creep in its early stages. Advanced stages can be detected using angle beam UT (SWUT* or PAUT*) or FMR. Destructive testing (removing a sample) to permit metallographic examination or stress-rupture testing may be applicable.

e) For inspection for environmental cracking due to DMWs initiating on or near the ID surface exposed to the corrosive environment, PT or WFMT (for magnetic materials) on the internal surface or angle beam UT (SWUT* or PAUT*) from the external surface, can be used.

***** DMWs (cladding, ferritic to austenitic butt welds, etc.) present challenges for inspecting due to beam/microstructure interactions (e.g. absorption, steering, and refraction). It is recommended that knowledge of grain size, specifically in austenitic stainless steels, and thickness are understood before applying UT techniques. Calibration should be done on similar materials (if not the same) as to be inspected. Inspection should be conducted by a technician experienced and knowledgeable with DMWs.

3.26.8 Related Mechanisms

Thermal fatigue (see 3.64), corrosion fatigue (see 3.21), creep and stress rupture (see 3.23), wet H_2S damage (see 3.67), and hydrogen stress cracking in HF (see 3.41).

3.26.9 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.

7. R.H. Ryder and C.F. Dahms, *Design Criteria for Dissimilar Metal Welds*, WRC Bulletin 350, Welding Research Council, Shaker Heights, OH, January 1990.

8. L.E. Penuela et al., "Analysis of Dissimilar Welds Exposed to High Temperature H_2/H_2S Conditions in a Hydrodesulfurizing (HDS) Unit," Paper No. 99383, *Corrosion/99*, NACE International, Houston, TX.

9. K.R. Lewis et al., "Assessment of Operating Limits for Critical Dissimilar Metal Welds in a Hydrocracker," Paper No. 01532, *Corrosion/2002*, NACE International, Houston, TX.

10. API 579-1/ASME FFS-1, *Fitness-For-Service*, American Petroleum Institute, Washington, DC, Second Edition, 2007.

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

12. API Subcommittee on Corrosion and Materials, Roundtable on Dissimilar Welds, April 17, 2007, Seattle, WA.

13. API Recommended Practice 582, *Welding Guidelines for the Chemical, Oil, and Gas Industries*, American Petroleum Institute, Washington, DC.

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

15. J.M. Mancini and M.A. Winters, "Cracking of a Dissimilar Metal Weld in Hydrogen Fluoride (HF) Acid Service," Paper No. 3794, *Corrosion/2014*, NACE International, Houston, TX.

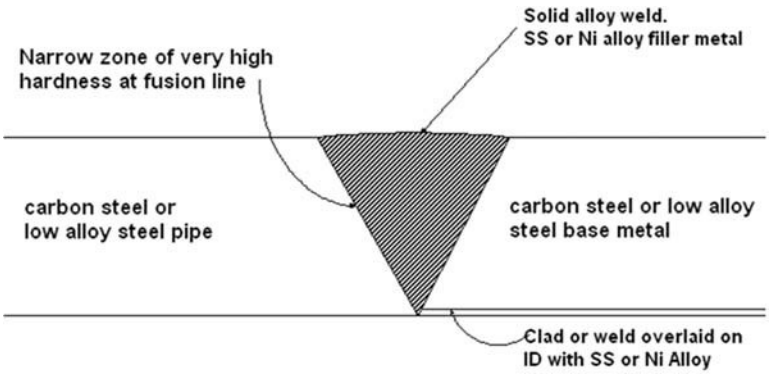
16. "Integrity of Ferritic/Austenitic Dissimilar Welded Joints in Hydrogen Service," NIL Report #IN-98-32.

17. R. Avery, "Guidelines for Welding Dissimilar Metals," NiDi Report 14 018, Nickel Development Institute, Toronto, ON, Canada, 1991.

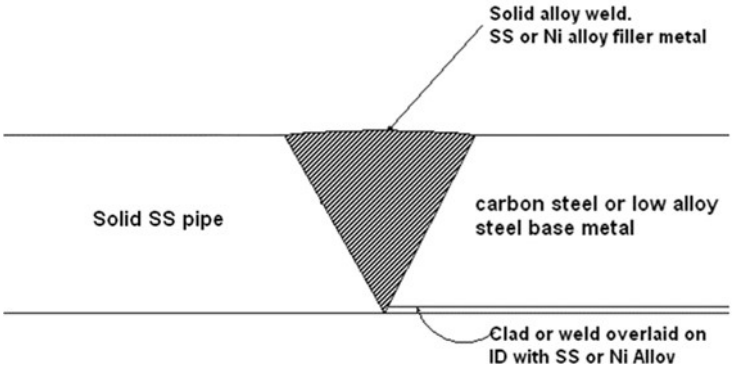
18. "Dissimilar-weld Failure Analysis and Development Program," EPRI Report CS-4252, Electric Power Research Institute, Palo Alto, CA, 1985.

Table 3-26-1—Coefficients of Thermal Expansion for Common Materials

Material	Coefficient (in./in./F x 10^{-6}) to 800 °F (425 °C)
CS	7.97
1Cr-½Mo	7.53
2¼Cr-1 Mo	7.53
300 series SS	10.05
Alloy 600	8



(a)



(b)

Figure 3-26-1—Two primary DMW configurations.
(a) Ferritic steel pipe (left) welded to clad or weld overlaid pipe.
(b) Solid stainless steel pipe (left) welded to clad or weld overlaid pipe.

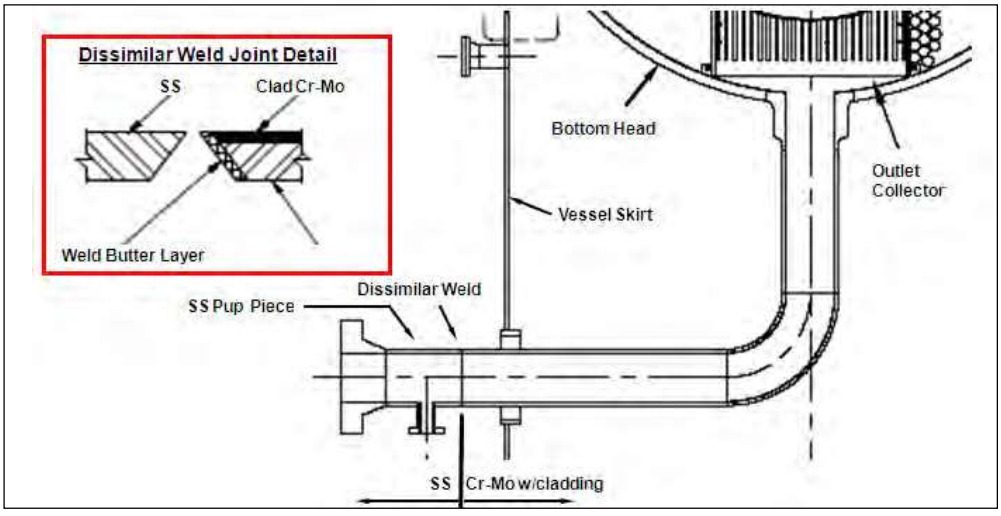


Figure 3-26-2—Schematic of typical weld detail used to join a solid stainless steel pipe to a clad or weld overlaid pipe. The sequence is as follows: (1) butter the weld bevel on the ferritic steel side, (2) perform PWHT of the ferritic side prior to making dissimilar weld, (3) complete the dissimilar weld using alloy filler metal, and (4) do not PWHT the completed dissimilar weld.

Figure 3-26-3—High-magnification photomicrograph of a DMW joining a ferritic alloy (SA213 T-22) used in high-temperature service. Creep cracks (black specks) can be observed in the ferritic alloy HAZs. Magnification 50X, etched.

Figure 3-26-4—Weld detail used to join a carbon steel elbow (bottom) to a weld overlaid pipe section (top) in high-pressure wet H_2S service. SSC occurred along the toe of the weld (arrow), in a narrow zone of high hardness.

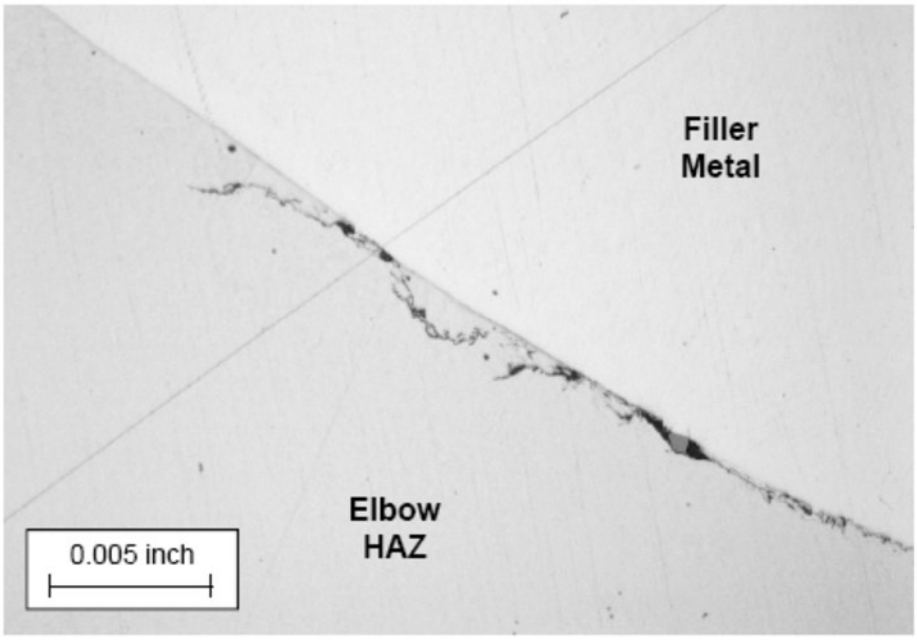


Figure 3-26-5—High-magnification photomicrograph of SSC in pipe section shown in Figure 3-25-4.

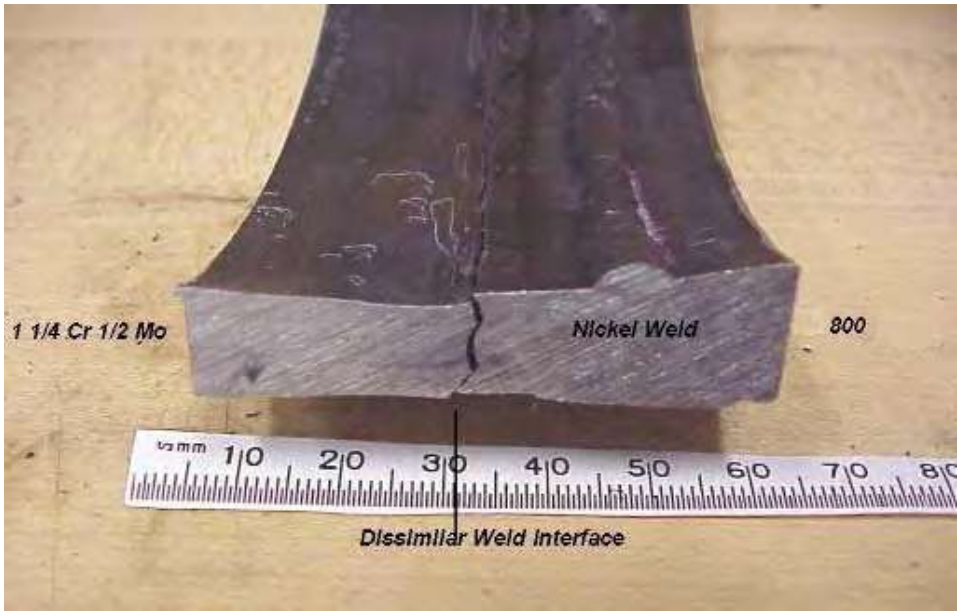


Figure 3-26-6—Failure of DMW joining 1.25Cr-0.5Mo to Alloy 800H in a hydro-dealkylation (HAD) reactor effluent exchanger. Crack propagation due to stresses driven at high of 875 °F (470 °C) and a hydrogen partial pressure of 280 psig (1.9 MPa).

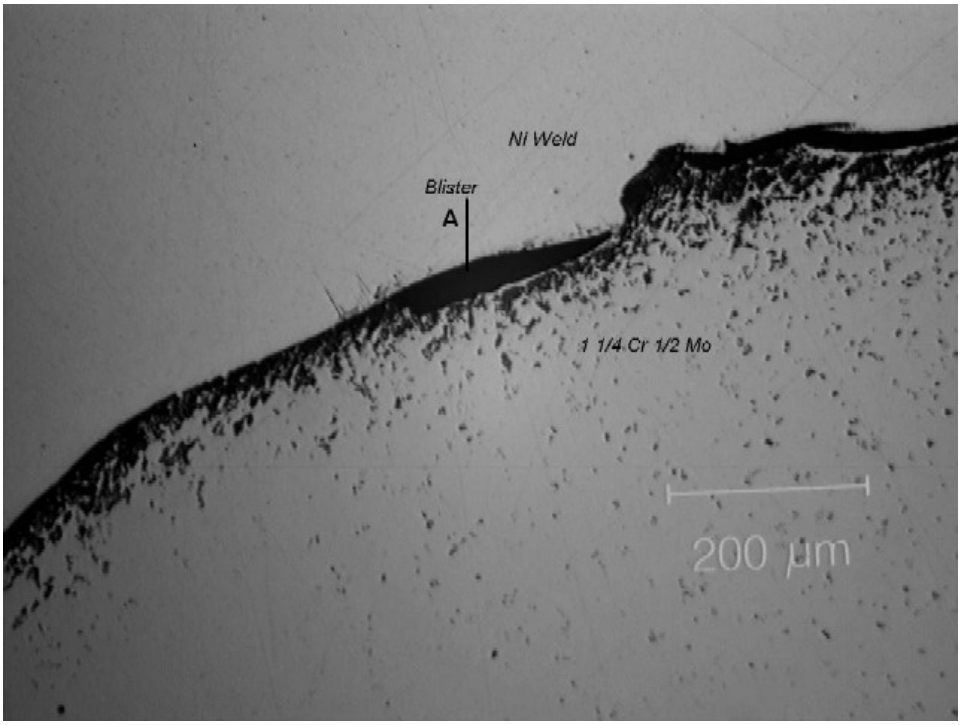


Figure 3-26-7—High-magnification photomicrograph of the crack in Figure 3-25-6 showing blistering and disbondment along the weld fusion line interface.

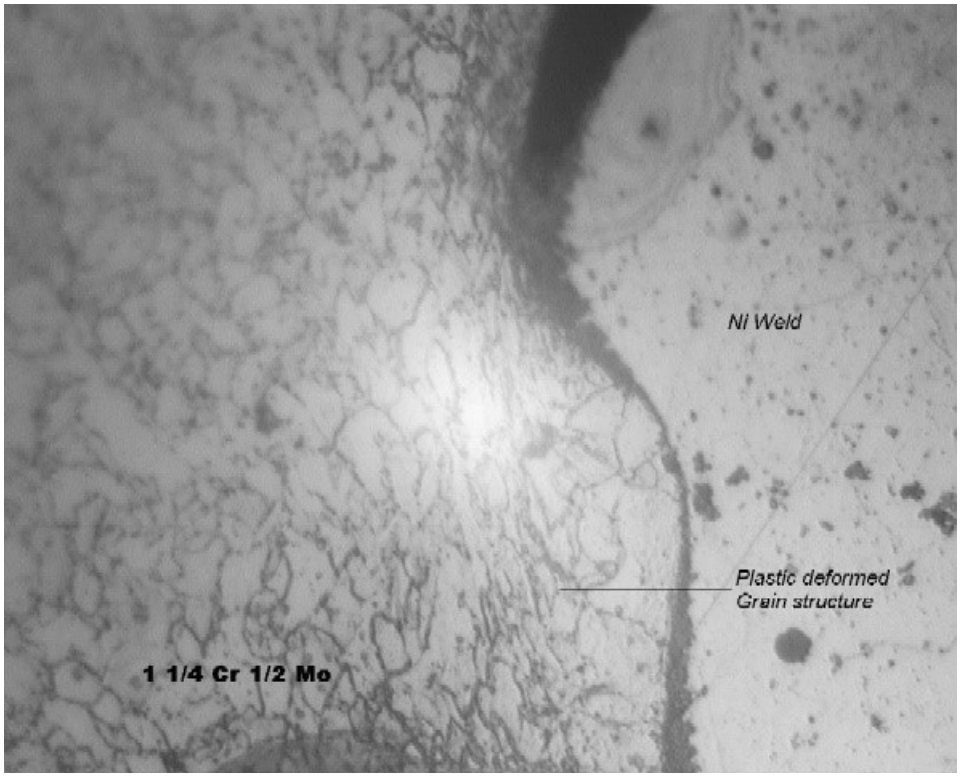


Figure 3-26-8—Higher-magnification photomicrograph of the crack shown above in Figure 3-25-6. Plastic deformation of the grain structure can be found at the vicinity of the blister.

Figure 3-26-9—Failure of nickel alloy DMW joining HP40 (Nb-modified) tube to 1.25Cr-0.5Mo flange in a steam-methane reformer due to cold hydrogen disbonding of the buttering layer. Process temperature 915 °F to 940 °F (490 °C to 505 °C), pressure 310 psig (2.15 MPa), H_2 content 10 % to 20 % (off-gas).

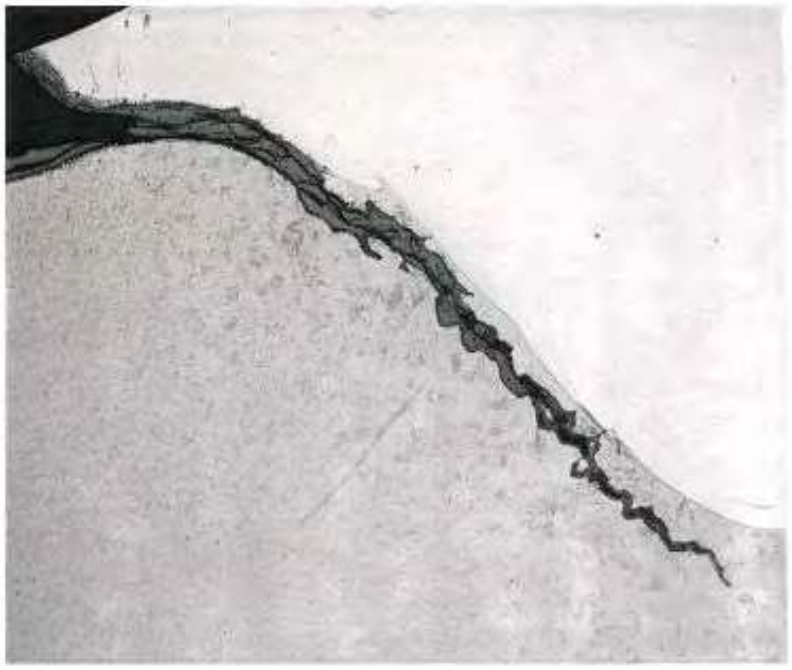


Figure 3-26-10—When both liquid phase coal ash corrosion and a DMW exists, stress-assisted corrosion of the 2.25Cr-1Mo HAZ may occur. Note that there is a lack of creep damage at the crack tip. Magnification 25X, etched.

Figure 3-26-11—A crack around the base of an Alloy 400 nozzle welded into a carbon steel vessel in HF acid service. (Reference 15)

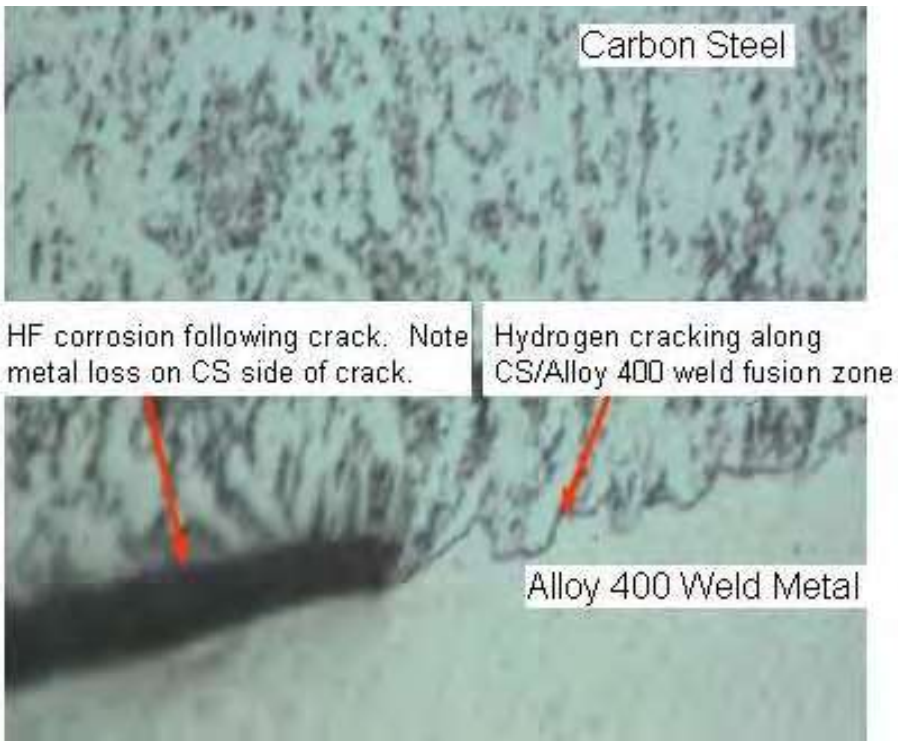


Figure 3-26-12—Photomicrograph showing crack propagation and corrosion in the Alloy 400 to carbon steel weld in Figure 3-25-11. (Reference 15)

3.27 Erosion/Erosion-Corrosion

3.27.1 Description of Damage

a) This subject covers a wide range of situations of material loss, from flowing solid particles alone or in a liquid or vapor stream physically abrading the material to material loss accelerated by the flow of corrosive liquid or vapor possibly combined with the velocity-assisted removal of a protective film or scale.

   1. Erosion is the mechanical removal of surface material as the result of relative movement between, or impact from, solids, liquids, vapor, or any combination thereof. It is typically found in services where solids are entrained in liquid or vapor streams such as slurries and fluidized solids. In refining, with the exception of water droplets in steam systems, it is unlikely that any flowing liquid or liquid impingement (without entrained solids) would be able to erode typical materials of construction without there also being a corrosion component present. The same can be said for gases, with the possible exception of steam cutting. However, see *Cavitation* (3.16).

   2. Erosion-corrosion is a description for the damage that occurs when particle erosion and/or high flow velocity contributes to corrosion by removing protective films or scales or otherwise accelerating the corrosion rate. This is also called velocity-assisted corrosion.

b) In most refinery erosion-corrosion situations, corrosion is the dominant consideration.

3.27.2 Affected Materials

All metals, but mostly carbon steel and copper alloys in refining. Refractories are also affected. Most commonly affected are materials without true passivity, where the corrosion rate is limited by a protective corrosion layer or inhibitive film.

3.27.3 Critical Factors

a) With solid particle mechanical erosion, metal loss rates will depend on the velocity and number of impacting particles (e.g. a low concentration of particles vs a slurry), as well as the size, shape, hardness, and density of the impacting particles, the hardness of the material subject to erosion, and the angle of impact.

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

   2. Increasing the hardness of the eroding metal component can reduce the rate of erosion damage. However, this may not be effective where corrosion plays a significant role.

b) For solids entrained in a liquid medium that also has a corrosion component, the same factors apply as with solid particle mechanical erosion described in Item a). However, with the solid particles removing any protective scales or other protective barrier on the metal surface, the rate of metal loss can be much greater than what is normally seen from the corrosion mechanism alone.

c) For corrosive liquid droplets entrained in a vapor, metal loss rates will depend on the velocity and number or rate of impacting droplets and the corrosivity of the liquid.

d) Many corrosive liquid environments will exhibit velocity-accelerated corrosion. In some cases, there is a threshold velocity below which corrosion is minimal but above which corrosion becomes significant. In other cases, there is no specific threshold; the highest corrosion rates simply occur where the velocity is greatest.

   1. Table 3-27-1 shows erosion-corrosion rates for a number of metals in seawater at different flow velocities. As the table illustrates, some alloys, particularly copper alloys, have an apparent threshold velocity above which the rate of metal loss increases significantly.

NOTE Increasing pipe thickness (schedule) will decrease the ID and increase the flow velocity, potentially increasing the corrosion rate.

e) In most cases, the more corrosive the environment is to a particular material, the greater will be the erosion-corrosion effect, especially where the erosion effect damages the stability of a protective film, scale, or other barrier upon which the metal depends for its corrosion resistance. Any factors that contribute to an increase in corrosivity of the environment, such as temperature, pH, etc., can increase susceptibility to erosion-corrosion metal loss.

3.27.4 Affected Units or Equipment

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

b) Erosion can be caused by gas-borne catalyst or coke particles or by particles carried by a liquid such as a slurry. This form of damage occurs as the result of catalyst movement in catalyst handling equipment (valves, cyclones, piping, reactors) and slurry piping in FCC reactor and regenerator systems. (Figure 3-27-1) It also occurs in coker heaters and coke handling equipment in both delayed and fluidized bed cokers. (Figure 3-27-2) And it causes “wear” on pumps (Figure 3-27-3), compressors, and other rotating equipment.

c) Hydroprocessing reactor effluent piping may be subject to erosion-corrosion by ammonium bisulfide. The metal loss is dependent on several factors including the ammonium bisulfide concentration, H_2S and NH_3 partial pressures, velocity and shear stress on the pipe wall, and corrosion resistance of the material. (See 3.5.)

d) Crude and vacuum unit piping and vessels exposed to naphthenic acids in some crude oils may suffer severe erosion-corrosion metal loss depending on the temperature, velocity, sulfur content, and naphthenic acid content. (See 3.46.)

e) Erosion-corrosion is common in acid alkylation systems.

f) Boiler water circuits can suffer accelerated corrosion from high-velocity flow, specifically known as “flow accelerated corrosion” (FAC). (See 3.9.)

g) High velocity also increases cooling water corrosion rates as well as corrosion rates in other corrosive media, as described in their respective sections in this document.

h) Erosion by water droplets in steam systems can be very damaging.

3.27.5 Appearance or Morphology of Damage

a) Erosion and erosion-corrosion are typically characterized by a localized loss in thickness in the form of grooves, gullies, waves, rounded holes, valleys, or simply a greater amount of thinning in a localized area such as the outer radius of a piping elbow. These losses often exhibit a directional pattern.

   1. There have been cases where the erosion or erosion-corrosion has occurred over a large enough surface area to cause a rupture.

b) In liquid lines containing particulate, low velocities, i.e. < around 5 fps (1.5 m/s), can allow solids to tumble to the bottom and cause erosion or erosion-corrosion in the 6 o’clock position.

c) Failures can occur in a relatively short time.

3.27.6 Prevention/Mitigation

a) Changes in shape, geometry, and materials can help mitigate erosion and erosion-corrosion. Examples include increasing the pipe diameter to reduce velocity, streamlining bends to reduce impingement, and using replaceable impingement baffles.

b) Improved resistance to mechanical erosion is usually achieved by increasing component hardness, e.g. using a harder alloy, hardfacing, or a surface-hardening treatment. Erosion-resistant refractories in cyclones and slide valves have successfully resisted erosion.

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

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

e) Refer to the relevant section of this document for methods to manage corrosion in erosion-corrosion prone environments (naphthenic acid, ammonium bisulfide, etc.).

f) Ensure proper operation to avoid water droplets in the steam system.

3.27.7 Inspection and Monitoring

a) Manual UT grids or automated scans can be used to determine the extent of erosion at susceptible areas, such as changes in direction, changes in diameter, or other turbulent areas. Randomly placed point UT readings may not be effective if they are not placed at the locations of potential susceptibility.

b) Profile RT can be used to detect areas of erosion but may not be able to determine the actual remaining wall thickness. UT thickness is normally used as a follow-up technique to quantify wall loss.

c) GWT can be used as a screening technique in certain applications where changes in piping direction will not impede the effectiveness of the examination.

d) Permanently mounted thickness monitoring sensors can be used.

e) Gouging or grooving along the bottom of a line and can be found by screening techniques [e.g. GWT, saturated low-frequency eddy current (SLOFEC), or X-ray crawler], UT scans or grids, or radiography.

f) Infrared thermography scans can be used on stream to detect refractory degradation (potentially due to erosion).

g) Specialized coupons can be used to determine if erosion is a potential concern.

h) Sampling of process streams for chemical analysis of solids and particulate size can help determine erosion potential within a system.

3.27.8 Related Mechanisms

Cavitation (3.16).

3.27.9 References

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

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

Table 3-27-1—Typical erosion-corrosion rates in seawater, mpy. (Reference 2)

Material	1 fps (tidal current)	4 fps (immersed in seawater flume)	27 fps (rotating disk)
Carbon steel	6	13	47
Cast iron	9	—	54
Silicon bronze	0.2	0.3	57
Admiralty brass	0.3	3	29
Hydraulic bronze	1	0.2	55
G bronze	1	0.3	46
Al bronze	1	—	44
Aluminum brass	0.4	—	19
90-10 Cu-Ni	1	—	16
70-30 Cu-Ni (0.05 %Fe)	0.3	—	32
70-30 Cu-Ni (0.5 % Fe)	<0.2	<0.2	6
Alloy 400	<0.2	<0.2	1
316 SS	0.2	0	<0.2
Alloy C-276	<0.2	—	0.05
Titanium	0	—	0

Figure 3-27-1—Erosion-corrosion of a 1¼Cr-½Mo, 300-lb valve flange on an FCC catalyst withdrawal line.

Figure 3-27-2—Erosion of a 9Cr-1Mo coker heater return bend as the result of high steam-air decoking velocity.

Figure 3-27-3—Erosion-corrosion of an ASTM A48 Class 30 cast iron impeller in a recycle water pump.

3.28 Ethanol Stress Corrosion Cracking

3.28.1 Description of Damage

Surface-initiated cracks caused by environmental cracking of carbon steel under the combined action of tensile stress and a fuel grade ethanol (FGE; ASTM D4806) or FGE/gasoline blend environment. Dissolved oxygen and the presence of variable stresses such as cyclic stress or component flexing increase the propensity for cracking.

3.28.2 Affected Materials

a) All grades of carbon steel are susceptible.

b) Ethanol SCC has not been reported in materials other than carbon steel, but general corrosion may be a concern with other materials including some alloys of aluminum, copper and copper alloys, lead, and zinc.

c) FGE and blends with gasoline may adversely affect nonmetallic materials (e.g. coatings and seals), causing swelling, hardness changes, etc.

3.28.3 Critical Factors

a) Several factors have been identified by field observations.

1. Stress may be applied or residual. Highly stressed, locally cold worked components, or components with stress concentrators are susceptible to cracking. Variable stresses, such as those produced by loading and unloading of tanks, have led to cracking in tank bottoms and floating roofs.

2. Cracking has been found to occur in FGE meeting ASTM D4806 specifications, including the water content requirement.

3. Corrosion inhibitors may be added to ethanol to prevent general corrosion in vehicle fuel systems, but their effect on SCC is not fully understood.

b) Other factors have been identified in controlled laboratory conditions using conservative slow strain rate test (SSRT) methods that stress the steel sample to failure. Evidence of SCC is based on the stress/strain behavior and an examination of the fracture surfaces.

1. Aeration (i.e. the dissolved oxygen content) of the ethanol appears to be the most important factor for determining ethanol SCC susceptibility. Cracking has not been found under deaerated conditions.

2. The maximum potential for ethanol SCC occurs within a narrow range of water content between 0.1 and 4.5 vol%.

3. Ethanol SCC has been found to occur in blends of FGE and gasoline containing as little as 20 vol% FGE.

4. Galvanic coupling of a new steel to corroded steel increases the likelihood of ethanol SCC.

5. Increasing the chloride content of the ethanol tends to increase the severity of cracking and changes the crack type from the mainly intergranular found in the field to transgranular cracking.

3.28.4 Affected Units or Equipment

a) Carbon steel storage tanks, rack piping, and associated equipment are susceptible to ethanol SCC. All grades of carbon steel are susceptible

b) Cracking has also been reported in a pipeline used to transport FGE to and from a terminal.

c) Ethanol SCC has not been reported in FGE manufacturers' equipment and tankage or in transportation equipment (barges, trucks, railcars).

d) Cracking has not been reported in equipment handling FGE after it has been blended with unleaded gasoline at end-use concentrations (10 vol% FGE). There has been one reported failure of an end-user E-85 tank.

3.28.5 Appearance or Morphology of Damage

a) Ethanol SCC is often found in the vicinity of welds and can appear as cracks that are parallel to the weld or transverse to the weld. (Figure 3-28-1 to Figure 3-28-8)

b) Cracks are typically tight and may be filled with corrosion product.

c) Ethanol SCC cracks are typically branched and intergranular, but transgranular or mixed-mode cracking has also been reported. Field failures tend to be intergranular, while laboratory testing has produced all crack morphologies. The cracking mode appears to depend on the chloride level, with an increased chloride content tending to shift the cracking from intergranular to transgranular or mixed mode.

d) Microstructure of materials subjected to ethanol SCC are typically ferrite, or ferrite and pearlite.

3.28.6 Prevention/Mitigation

a) The likelihood of ethanol SCC can be reduced though PWHT (when possible) or by applying coatings.

b) Avoid designs with highly localized tensile stresses.

c) Avoid the usage of lap seam welds (where practical) that may concentrate strain in components.

d) Minimize cold working during fabrication and the use of springs and other devices (e.g. for floating roof components) made using cold-worked steel.

3.28.7 Inspection and Monitoring

Ethanol SCC is difficult to predict and detect, and as is generally the case for SCC mechanisms, routine inspection for ethanol SCC is not an effective way to manage the issue. Efforts need to be focused on prevention.

a) Inspection for ethanol SCC is generally performed where cracking is already suspected or to determine the extent of cracking after a leak has occurred. It is especially difficult to detect prior to leaking in piping and equipment where there is no access to the internal surface. When inspection is performed, it should be focused on highly stressed areas, such as weld HAZs and the area immediately adjacent to the HAZ, highly cold worked areas, and highly stressed areas.

b) It is difficult to visually detect ethanol SCC because the cracks are typically tight and filled with corrosion product. Some small leaks may occur before an ethanol crack can be visually detected.

c) WFMT is the preferred method for detecting ethanol SCC. Methods for ethanol SCC inspection are similar to those used for detecting other types of SCC.

d) Angle beam UT (SWUT or PAUT) can detect internal SCC from the external surface and thus can be used in instances where internal access for WFMT is not possible. These UT methods may also be used for estimating the depth of cracking.

e) ACFM is an effective method for SCC detection and requires less surface preparation than WFMT.

f) ECT is unproven as a method for detection of ethanol SCC.

g) AET has had some success in detecting, locating, and monitoring SCC growth. However, results sometimes can be inconclusive and quality AET data may be difficult to obtain, and there is no industry track record of use of AET to detect ethanol SCC.

3.28.8 Related Mechanisms

Ethanol SCC is assumed to be similar to SCC reported in methanol and various alkaline aqueous solutions, e.g. amine SCC (3.3), carbonate SCC (3.12), and caustic SCC (3.15).

3.28.9 References

1. API Technical Report 939-D, *Stress Corrosion Cracking of Carbon Steel in Fuel-grade Ethanol: Review, Experience Survey, Field Monitoring, and Laboratory Testing*, Second Edition, May 2007, American Petroleum Institute, Washington, DC.

2. API Bulletin 939-E, *Identification, Repair, and Mitigation of Cracking of Steel Equipment in Fuel Ethanol Service*, Second Edition, August 2013, American Petroleum Institute, Washington, DC.

3. ASTM D4806, *Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel*, ASTM International, West Conshohocken, PA.

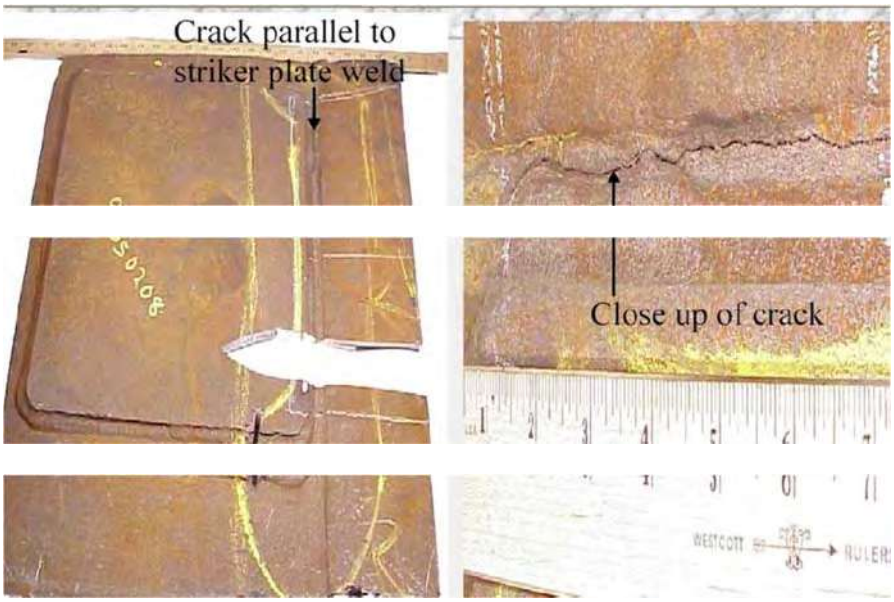


**Figure 3-28-1—Ethanol SCC in a steel tank bottom.
Note crack running parallel to fillet weld in striker plate.**

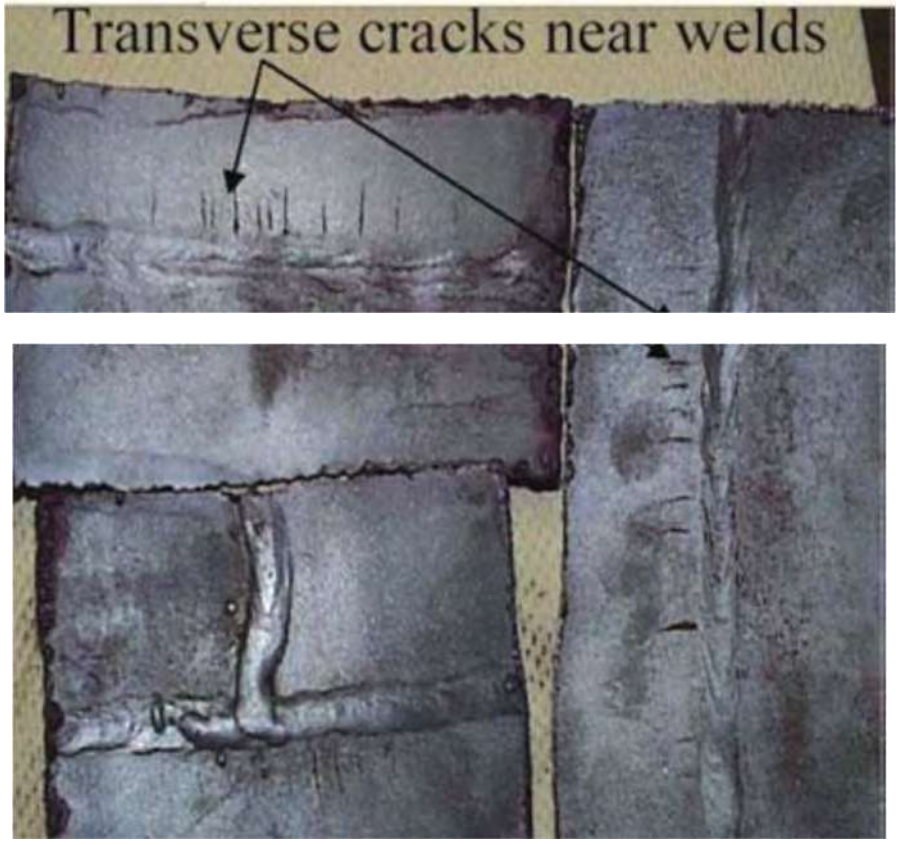


Figure 3-28-2—Ethanol SCC in a steel air eliminator vessel. Note cracks running perpendicular to the weld.

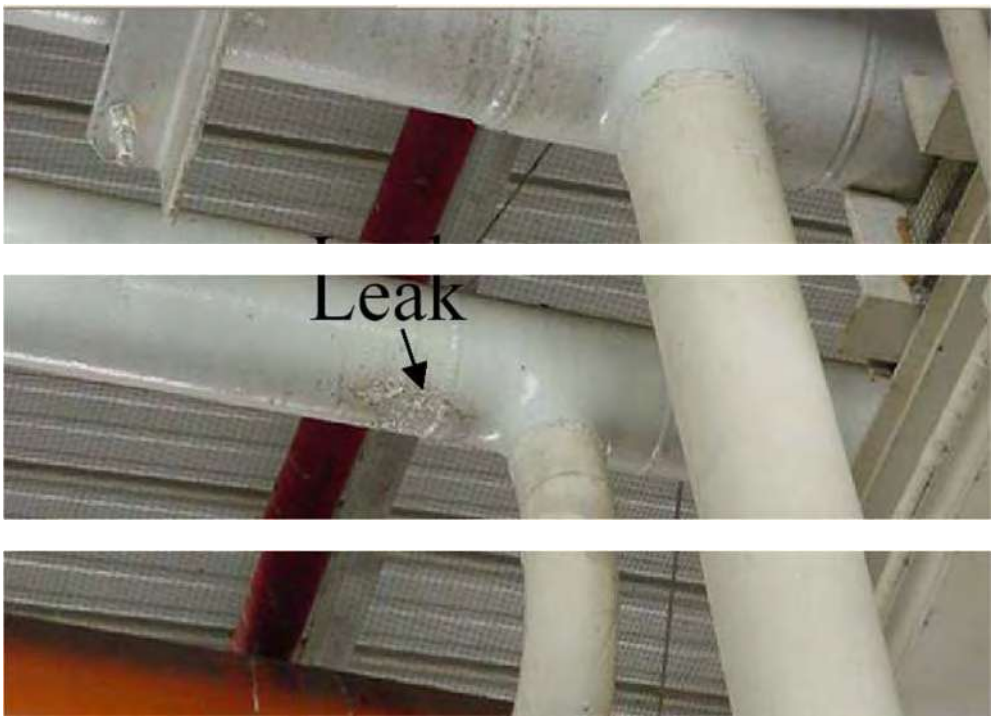


Figure 3-28-3—A leak in piping resulting from an ethanol stress corrosion crack adjacent to the weld.

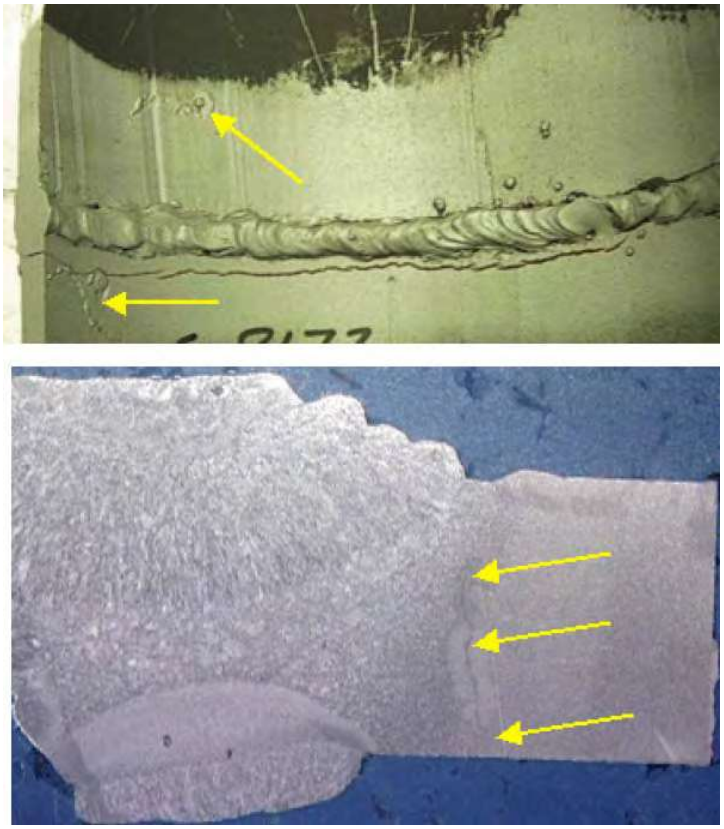


Figure 3-28-4—Ethanol SCC in steel pipe from a loading rack supply line. The top figure shows a 7-in.-long crack parallel to the weld root on the pipe ID surface. The bottom picture is a cross section of the above crack showing initiation outside the weld HAZ on the pipe's inside surface (Nital etch).

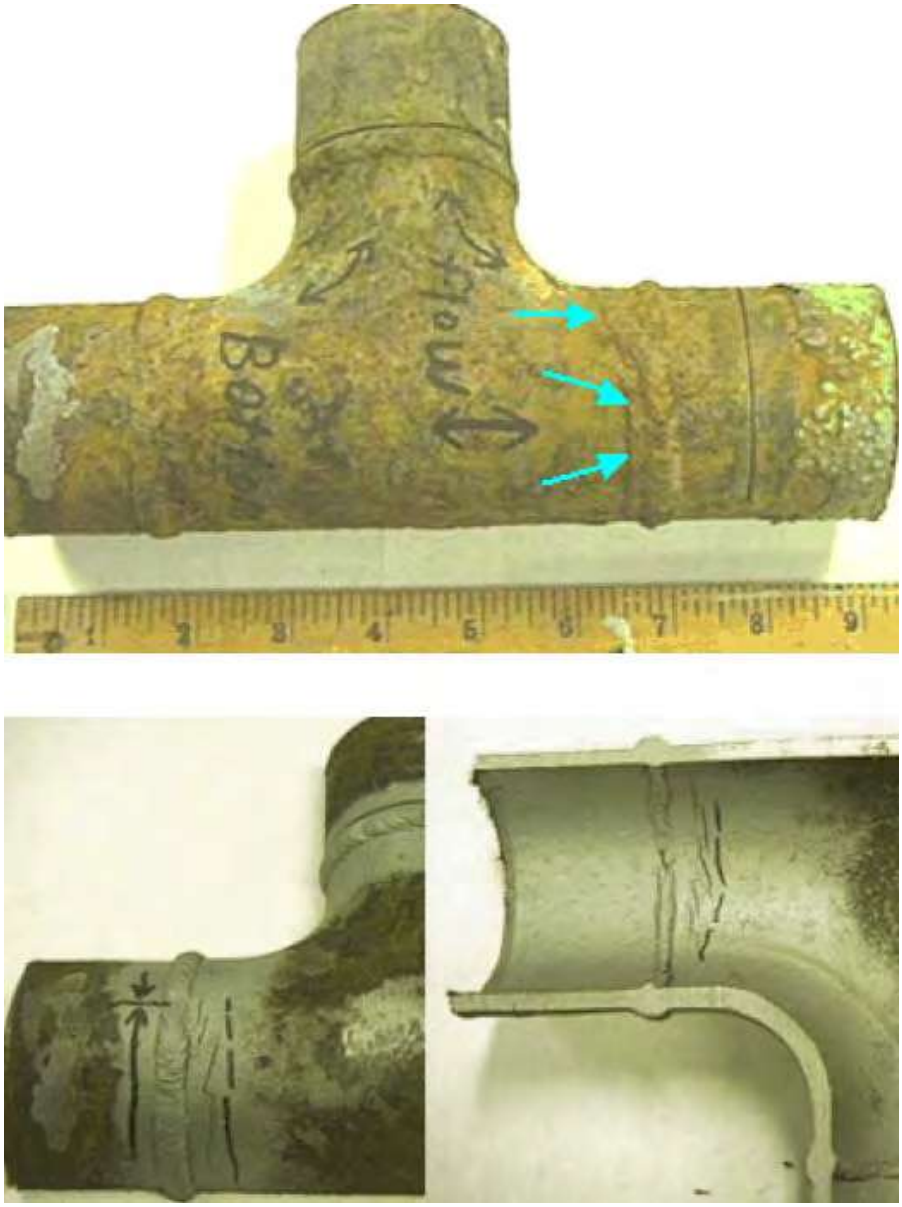


Figure 3-28-5—Ethanol SCC of steel piping in a fuel ethanol system return line/tank transfer line. The top picture shows the crack parallels the pipe-to-tee circumferential weld. The bottom picture shows the inside and outside of the pipe after splitting and cleaning the weld area. Parallel SCC cracks are clearly visible adjacent to the weld.

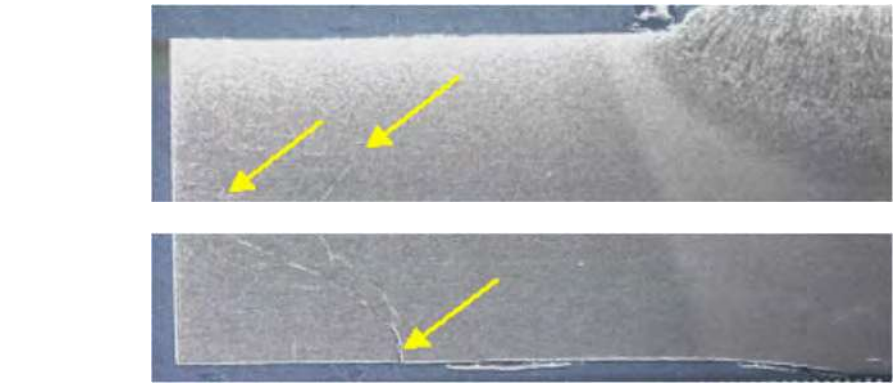


Figure 3-28-6—The top picture shows cracking initiating in the base metal on the ID of a section of piping adjacent to the weld. The bottom picture is a high-magnification photomicrograph of the crack above illustrating the predominately intergranular nature of the cracking. (Magnification 380X, Nital etch.)

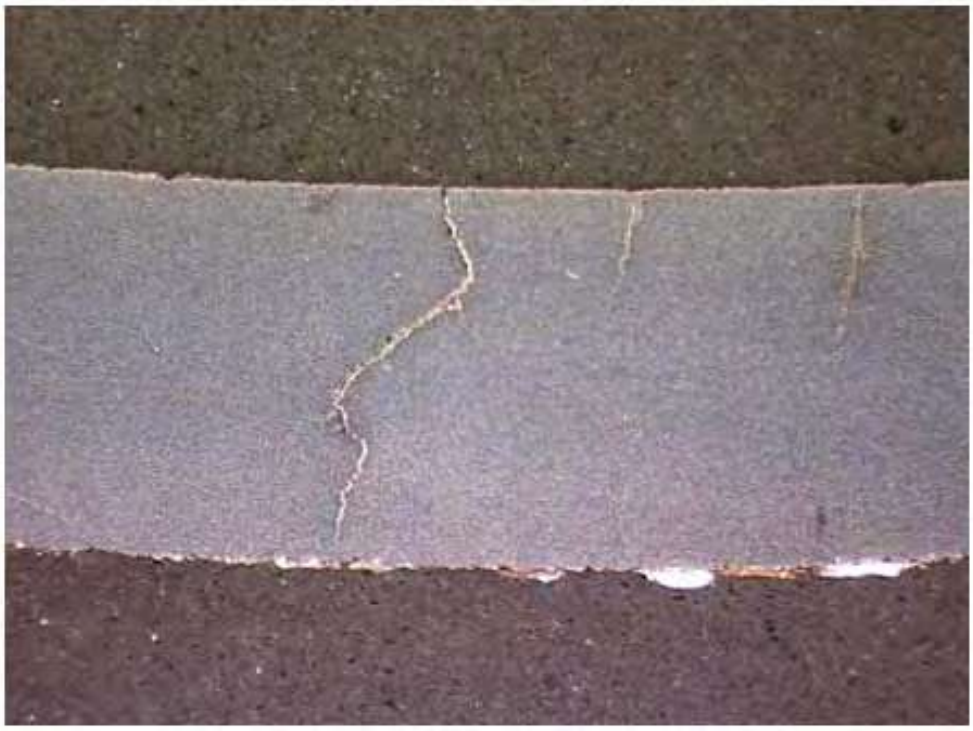


Figure 3-28-7—Transverse cross section of a piping section exposed to fuel ethanol showing multiple crack initiation sites characteristics of SCC.

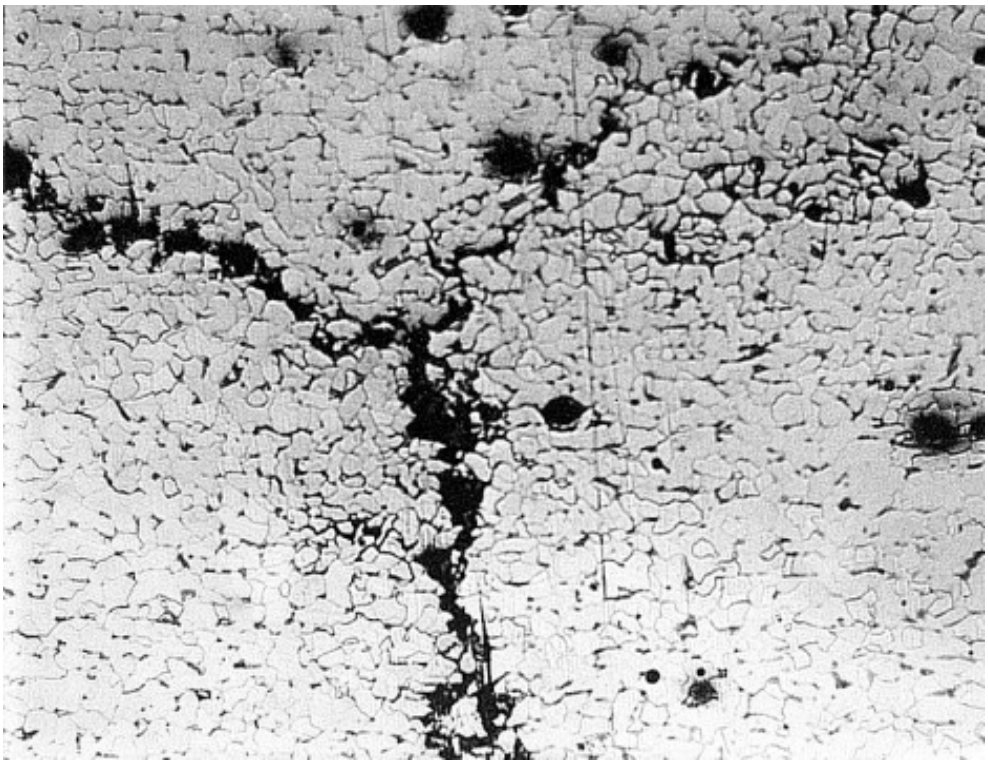


Figure 3-28-8—Photomicrograph of ethanol SCC in a steel tank bottom showing highly branched, intergranular cracks at 100X magnification.

3.29 Flue Gas Dew Point Corrosion

3.29.1 Description of Damage

Sulfur, nitrogen, and chlorine species in fuel will form sulfur dioxide, sulfur trioxide, nitrogen dioxide, and hydrogen chloride gas to go along with the CO_2 within the combustion products. At temperatures at or below the dew point, these gases and the water vapor in the flue gas will condense to form sulfurous acid, sulfuric acid, nitric acid, hydrochloric acid, and carbonic acid, which can lead to severe corrosion.

3.29.2 Affected Materials

Carbon steel, low-alloy steels, and 300 series SS.

3.29.3 Critical Factors

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

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

c) The dew point of sulfuric acid depends on the concentration of sulfur trioxide in the flue gas but is typically about 280 °F (140 °C).

d) Dew points for sulfurous, hydrochloric, nitric, and carbonic acids depend on the concentrations of SO_2, HCl, NO_2, and CO_2 and on the water content of the flue gas, but they occur typically at temperatures lower than the water dew point, 212 °F (100 °C). Hence, corrosion by these acids gases is expected to occur only when surface temperatures reach or go below the water dew point.

3.29.4 Affected Units or Equipment

a) Sulfur recovery unit (SRU) incinerators and FCC unit regenerator flue gas systems, as well as fired process heaters and boilers that burn fuels containing sulfur, nitrogen, or chloride have the potential for acid dew point corrosion in the economizer sections and in the stacks.

b) Similar damage occurs in oil-fired boilers when the units are water-washed to remove ash if the final rinse does not neutralize the acid salts.

c) Heat-recovery steam generators (HRSGs) that have 300 series SS feedwater heaters may suffer chloride-induced SCC from the gas side (OD) when the temperature of the inlet water is below the dew point of hydrochloric acid.

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

3.29.5 Appearance or Morphology of Damage

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

b) For the 300 series SS feedwater heaters in HRSGs, SCC will have surface-breaking cracks and the general appearance will be somewhat crazed.

3.29.6 Prevention/Mitigation

a) The metallic surfaces at the back end of the boilers and fired heaters and stacks should be kept at least 10 °F (6 °C) above the dew point temperature of sulfuric acid (the highest dew point of the condensable acid gases).

b) For HRSGs, avoid the use of 300 series SS in the feedwater heaters if the environment is likely to contain chlorides.

c) When water washing to remove ash, sodium carbonate should be added to the final rinse as an alkaline solution to neutralize the acidic ash constituents.

3.29.7 Inspection and Monitoring

Because flue gas corrosion occurs on tubes nearest the stack, which are typically finned tubes, the fins interfere with most inspection techniques that might be used on other heater and boiler tubes.

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

b) To obtain UT thickness readings of finned tubes, a section of fins normally must be removed.

c) Permanently mounted thickness monitoring sensors can be used.

d) SCC of 300 series SS can be found using VT, PT, and ECT inspection.

e) In the case where the tubes and fins are the same material, a VT of the fins will provide an indication if the damage mechanism is present.

f) RT can be utilized to obtain thickness readings, as geometry allows.

g) VT inside of stacks using a remote camera may be possible in some configurations.

3.29.8 Related Mechanisms

Hydrochloric acid corrosion (3.37), sulfuric acid corrosion, (3.62), and Cl^- SCC (3.17).

3.29.9 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.

3.30 Fuel Ash Corrosion

3.30.1 Description of Damage

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

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

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

3.30.2 Affected Materials

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

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

3.30.3 Critical Factors

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

b) Sodium (Na) and vanadium (V) content are very important. Typically, a combined concentration of Na and V above 50 ppm will cause damage.

c) Corrosion occurs by this mechanism only if the metal temperature is high enough to melt the deposits and form the molten slag. It is most severe where the temperatures are the highest.

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

e) The molten slags are different for oil ash vs coal ash. They are also different for waterwall tube corrosion.

1. For oil ash, the liquid species are mixtures of vanadium pentoxide and sodium oxide, or vanadium pentoxide and sodium sulfate. Depending on the precise composition, melting points below 1000 °F (540 °C) are possible.

2. For coal ash, superheater and reheater corrosion is caused by sodium and potassium iron trisulfates that melt between 1030 °F and 1130 °F (545 °C and 610 °C), depending on the ratio of sodium and potassium. Reducing (low-oxygen) conditions, i.e. a flue gas rich in carbon monoxide, hydrogen sulfide, and hydrogen, will increase corrosion rates 2 to 5 times compared to oxidizing (oxygen-rich) conditions.

3. For waterwall tube corrosion, the liquid species are mixtures of sodium and potassium pyrosulfates that have melting points as low as 700 °F (370 °C).

4. Unburned coal particles also add carbon to the fly ash deposits and provide a reducing environment on the tube surface where corrosion occurs. Carburization of the tube surface, especially on austenitic alloys, will decrease corrosion resistance and increase tube wastage rates.

3.30.4 Affected Units or Equipment

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

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

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

d) Some gas turbines suffer blade corrosion when switched over to burning fuel oil.

e) In some cases, coking of heater tubes may cause operators to increase heat flux that may push some components above the threshold temperature where fuel ash corrosion is possible.

f) Since the melting points of these liquid species are around 1000 °F (540 °C) and higher in the superheaters and reheaters, any unit that has metal temperatures above the melting point of the sulfates may have the problem.

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

h) For waterwall tubes, if the temperature can be maintained below the melting point of the pyrosulfates [i.e. below 700 °F (370 °C)], damage will be minimized. Thus, steam-generating pressures below about 1800 psi (12.5 MPa) are nearly immune.

3.30.5 Appearance or Morphology of Damage

a) Oil ash corrosion is manifested as severe metal loss associated with slagging. In some cases, corrosion rates of 100 mpy to 1000 mpy (2.5 mm/yr to 25 mm/yr) may be experienced.

b) With oil ash, corrosion may result in a corroded surface with numerous deep round pits. (Figure 3-30-1 and Figure 3-30-2)

1. There are also representative photos of fuel ash and coal ash corrosion in Reference 4.

c) The liquified corrodents can melt together during the corrosion process and form a hard, glassy, tenacious scale.

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

e) Metallographic examination and deposit-analysis techniques can be used to verify the presence of fuel ash corrosion. Oil ash deposit will often appear in at least two distinct layers. The deposit adjacent to the component will have a dark gray or black appearance at room temperature.

f) For waterwall tubes, thermal fatigue cracks can occur in conjunction with the fuel ash corrosion. (Figure 3-30-3) The cracks are predominantly circumferential and, to a lesser extent, axial. The overall appearance on the waterwalls is one of circumferential grooving.

1. After the liquid ash layer develops, the “slush” can only hold a certain weight of ash. When the weight is excessive, the slag is shed, exposing a bare, uninsulated tube to the heat flux of the firebox. The temperatures will spike on waterwall tubes, by perhaps 100 °F (55 °C). Repetitive cycles can result in thermal fatigue cracking.

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

3. After removal of the corrosion scale on superheaters and reheaters, the steel can have an alligator-hide appearance. (Figure 3-30-4) This, as well as the circumferential cracking on waterwalls in coal-fired boilers, is caused by a similar mechanism.

3.30.6 Prevention/Mitigation

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

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

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

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

e) Maintaining the combined sodium plus vanadium content below 50 ppm will control the damage.

3.30.7 Inspection and Monitoring

a) VT is usually sufficient to detect fuel ash corrosion.

b) Metal loss is likely to be severe, and the presence of a slag will be apparent.

NOTE Tubes may need to be grit blasted in order to remove the tenacious, glass-like deposit.

c) UT may be useful to measure loss of thickness.

3.30.8 Related Mechanisms

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

3.30.9 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.

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

8. E. Mirabel et al., “Fireside Carburization of Stainless Steel Furnace Tubes,” Paper No. 99080, *Corrosion/99*, NACE International, Houston, TX.

Figure 3-30-1—Type 316Ti stainless steel roof tube in a heavy fuel oil-burning vacuum heater that failed by fuel ash corrosion. The tube perforated at this location.

Figure 3-30-2—A closer view of the pitting appearance of the attack on the tube surface shown in Figure 3-29-1.

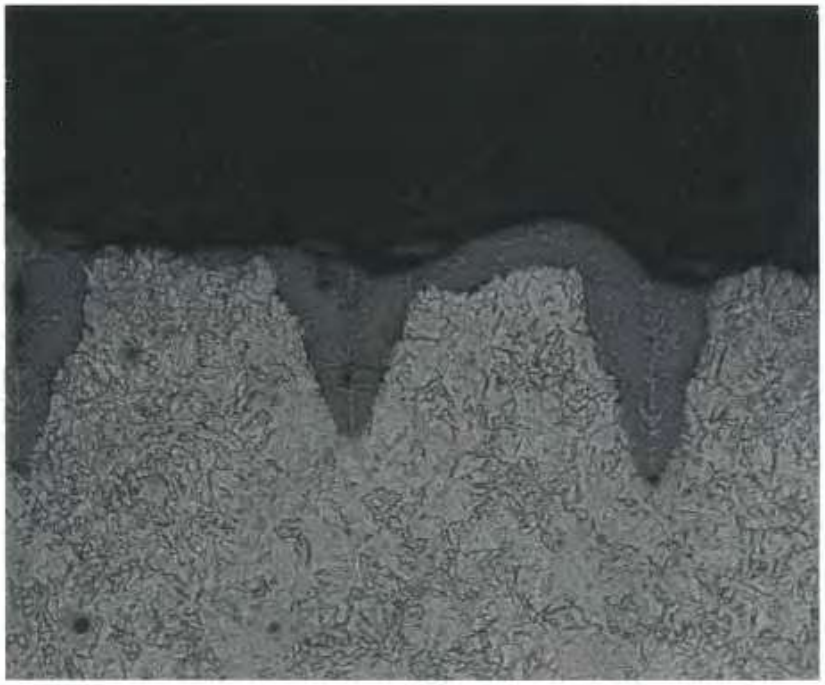


Figure 3-30-3—In cross section, the surface grooving on waterwall tubes that occurs in conjunction with fuel ash corrosion appears as broad, V-shaped corrosion fatigue cracks. Magnification 100X, etched.

Figure 3-30-4—The "alligator hide" morphology of liquid coal-ash corrosion is evident on the metal surface when the dense, glassy deposit is removed. Magnification 2.4X.

3.31 Galvanic Corrosion

3.31.1 Description of Damage

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

3.31.2 Affected Material

All metals with the exception of most noble metals.

3.31.3 Critical Factors

a) For galvanic corrosion, three conditions must be met.

1. There must be two (or at least two) different metals with different electrochemical potentials.

2. The dissimilar metals must be electrically coupled together, either by being directly in contact with or connected to each other or connected by a wire or other conductor. One of these metals is known as the anode and the other is the cathode.

3. Both metals must be immersed or in contact with the same, continuous electrolyte, i.e. a fluid that can conduct electric current. Moisture or a separate water phase is usually required for the fluid to have enough conductivity.

b) The more noble material (the cathode) is protected by sacrificial corrosion of the more active material (the anode). The anode corrodes at a higher rate than it would if it were not connected to the cathode.

c) A typical listing of the relative position on the active to noble scale of alloys in seawater is shown in Table 3-31-1.

d) The farther the alloys are apart in the table, the higher the driving force for corrosion.

e) The relative amount of surface area exposed to the electrolyte between the more active anode material and the more noble cathode material has a significant affect.

1. If there is a small anode-to-cathode exposed surface area ratio, the corrosion rate of the anode can be very high.

2. If there is a large anode-to-cathode surface area ratio, the corrosion rate of the anode will be less affected.

f) The same metal may act as either an anode or a cathode in different situations due to the effect of surface films, scale, and/or the properties of the electrolyte on its electrochemical potential in that particular situation (e.g. old steel pipe connected to new steel pipe).

g) The same electrochemical coupling of different metals that leads to galvanic corrosion is put to beneficial effect in the form of cathodic protection when a more active sacrificial material, e.g. an aluminum or magnesium anode, is coupled to a less active (more noble) metal, e.g. carbon steel. This is the principle behind galvanized steel, where the zinc (Zn) coating corrodes preferentially to protect the underlying carbon steel. [If there is a break in the galvanizing coating, the resulting large anode to small cathode area prevents accelerated corrosion of the steel, while the Zn coating (anode) continues to cathodically protect the exposed steel.] This Zn-to-steel anode-to-cathode relationship appears to reverse in aerated water at temperatures above about 150 °F (65 °C). This is because the corrosion products and scale that form on the surface of the galvanizing make the surface more noble than steel. However, the relative positions of the open circuit potentials of the two metals do not actually switch at any temperature.

3.31.4 Affected Units or Equipment

a) Galvanic corrosion can occur in any unit where different metals are coupled in a conductive fluid. Heat exchangers are susceptible if the tube material is different from the tubesheet and/or baffles, particularly if saltwater cooling is utilized.

b) Buried piping and ship hulls are also typical locations for galvanic corrosion.

3.31.5 Appearance or Morphology of Damage

a) Damage occurs where two different materials are joined at welded, bolted, or rolled connections.

b) The more active material can suffer generalized loss in thickness or more aggressive localized loss adjacent to the point of connection, with the appearance of crevice, grooving, or pitting corrosion, depending on the driving force, conductivity of the electrolyte, and the relative anode/cathode area ratio. (Figure 3-31-1 and Figure 3-31-2)

3.31.6 Prevention/Mitigation

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

b) Coupling of different metals in a conductive fluid should be avoided; however, the galvanic effect will be minimized if the anode/cathode surface area ratio is favorable.

c) If a coating is to be used to mitigate corrosion of a galvanic couple, care must be exercised. If only the active material were coated, a small anode-to-cathode area ratio would exist wherever a coating defect or damage exposed bare anode metal, which would greatly accelerate corrosion of the anode at the break in the coating. Therefore, the exposed areas of both the anode and the cathode should be coated. If only one can be coated, the more noble cathode material should be the one coated. In this case the coating will not protect the anode, but at least the acceleration of the corrosion rate caused by the galvanic couple will be minimized or eliminated.

d) For piping, specially designed electric insulating bolt sleeves and gaskets (i.e. isolation flanges) can eliminate the electrical connection.

e) Sacrificial anodes are sometimes installed in carbon steel cooling water exchanger channels to control channel and tubesheet corrosion, particularly where Cu-alloy tubes such as admiralty brass are used.

3.31.7 Inspection and Monitoring

a) VT and UT thickness gauging are effective methods for detecting galvanic corrosion.

1. VT may indicate loss of the more anodic material by displaying oxidized material before it is cleaned.

2. UT thickness measurement techniques have been effective in determining the amount of loss in the more anodic material.

b) Permanently mounted thickness monitoring sensors can be used.

c) The damage could also be hidden underneath a bolt or rivet head.

1. An initial “total picture” examination may be necessary to understand the nature of joints under consideration. In the case of bolt heads or rivets, an angled beam technique may be needed to evaluate the hidden loss under the head of the fastener.

3.31.8 Related Mechanisms

Concentration cell corrosion (3.19), soil corrosion (3.57), DMW cracking (3.26), and titanium hydriding (3.66).

3.31.9 References

1. *Corrosion Basics—An Introduction*, NACE International, Houston, TX, 1984, pp. 33–37.

Table 3-31-1—Galvanic Series in Seawater. (Reference 1)

Corroded End—Anode—More Active
Magnesium
Magnesium alloys
Zinc
Aluminum
Aluminum alloys
Steel
Cast iron
Type 410 SS (active state)
Ni-resist
Type 304 SS (active state)
Type 316 SS (active state)
Lead
Tin
Nickel
Brass
Copper
Bronze
Copper-nickel
Monel
Nickel (passive state)
Type 410 SS (passive state)
Type 304 SS (passive state)
Type 316 SS (passive state)
Titanium
Graphite
Gold
Platinum
Protected End—Cathode—More Noble

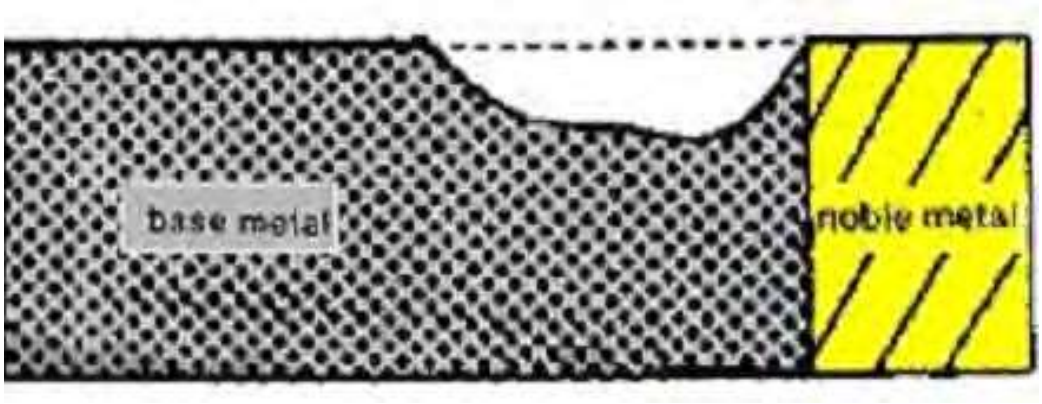


Figure 3-31-1—Preferential galvanic corrosion of the more active of the two materials.

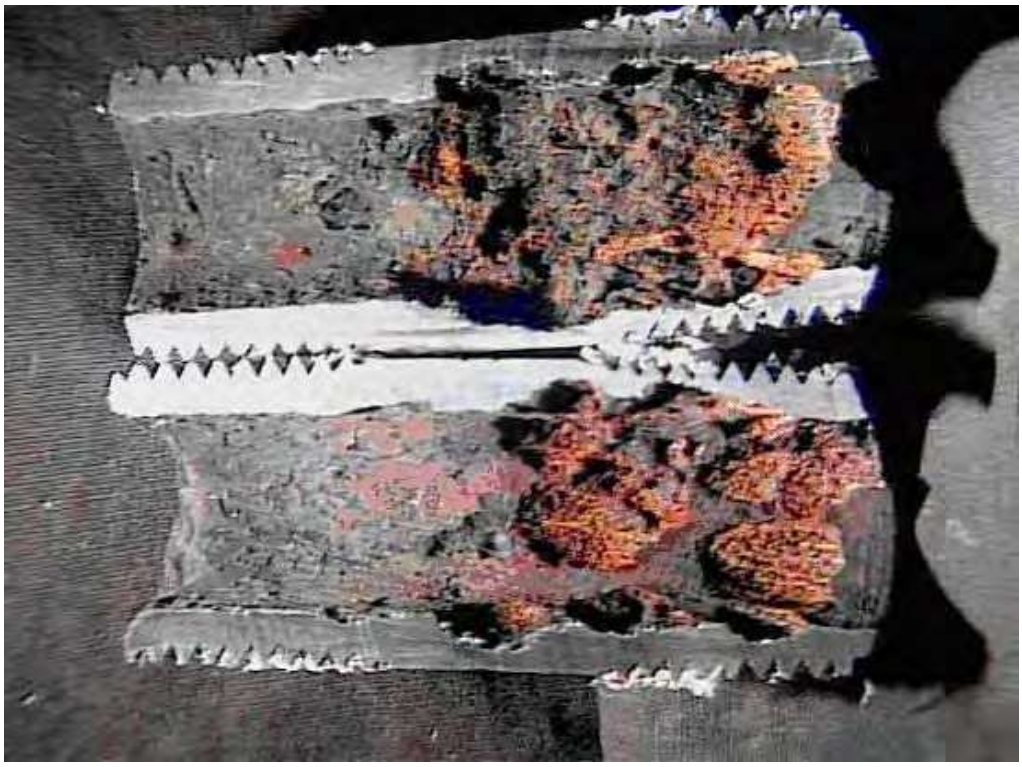


Figure 3-31-2—Galvanic corrosion of a carbon steel nipple in a stainless steel vessel in warm water service.

3.32 Gaseous Oxygen-enhanced Ignition and Combustion

3.32.1 Description of Damage

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

3.32.2 Affected Materials

a) Carbon steels and low-alloy steels are flammable in oxygen-rich environments greater than about 15 psig (0.1 MPa) oxygen pressure. However, with special precautions, these materials are safely used in high-pressure oxygen.

b) 300 series SS have better resistance to low-pressure oxygen-rich environments and are generally difficult to ignite at oxygen pressures below about 200 psig (1.4 MPa).

c) Copper alloys (with > 55 % copper) and nickel alloys (with > 50 % nickel) are very fire resistant and are generally considered non-flammable. Because of their excellent oxygen “compatibility,” they are often selected for impingement and turbulent services such as valves and instrumentation. (But, see Figure 3-32-5.) Alloy 400 is highly resistant.

d) Although widely used for oxygen cylinders and in oxygen manufacturing plants, aluminum is usually avoided for flowing oxygen. Aluminum may ignite at ambient temperature with low levels of ignition energy. If ignited, it burns quickly and with a large energy release.

e) The easiest materials to ignite are plastics, elastomers, and hydrocarbon lubricants, and their use is minimized in oxygen systems.

f) Titanium and titanium alloys are generally avoided in oxygen and oxygen-rich service, because they have low ignition energies and release a large amount of energy during combustion. Tests indicate that titanium can sustain combustion at oxygen pressure as low as 1 psia (7 kPa). Most industry documents caution against the use of titanium in oxygen systems. (References 5 and 6)

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

3.32.3 Critical Factors

Many factors contribute to the likelihood of combustion and ignition in oxygen services. They include system pressure, line velocity, temperature, system cleanliness, piping configuration, component thickness, system design, oxygen content of the stream, and ignition energy. (A unique aspect of oxygen-rich systems is that the source of energy does not need to be a spark or flame; the source may be the presence of ignition energy.)

a) Pressure in an oxygen system affects the potential ignition mechanisms of metallic systems. Systems operating below 500 psi are considered less severe than systems operating above 500 psi.

   1. High-purity oxygen systems over 500 psi are considered to have a severe effect on metal burning reactions because the amount of energy needed to start ignition is lower than the energy required in low-pressure systems.

   2. High-purity oxygen systems below 500 psi are considered to have a moderate or mild effect on metal burning reactions.

b) The primary concern with high-velocity oxygen flow is the entrainment of particulates in the stream. High-velocity particulates can create friction or impinge on a surface, such as at a pipe bend. Friction or impingement could result in ignition of the metal. Oxygen velocities in carbon steel and stainless steel piping should comply with industry limits as shown in Reference 1. Allowable velocity is a function of pressure and flow condition (direct impingement or non-impingement).

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

1. Commonly used metals in high-purity oxygen systems may have an autoignition temperature as low as 1650 °F (900 °C).

2. Nonmetallic items in high-purity oxygen systems may have an autoignition temperature as low as 300 °F (150 °C).

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

e) The piping configuration, or layout, could create impingement areas such as at elbows, tees, or valves. These components pose a higher risk of ignition than straight pipe.

1. Particles in the flowing oxygen can strike these areas and cause ignition.

2. Operation of valves and regulators (opening/closing) causes high turbulence and impingement.

3. Material selection for components in impact or impingement prone locations and high-turbulence areas is critical.

4. Only items selected and cleaned specifically for oxygen service should be used in high-purity oxygen systems.

f) Thin components or components with a high ratio of surface area to material volume provide a geometry that is susceptible to ignition of the metal. Examples include mist eliminators, demister pads, steel wool, and structured packing. (Figure 3-32-4)

g) The system design must compensate for the effect of items like mechanical impact, heat of combustion, kindling effect of contaminants, system resonance, fresh metal exposure, heat of compression, and turbulence. Reference 7 provides detailed information on the compatibility of various metals in oxygen-rich environments.

h) The oxygen content has two effects. As the concentration of oxygen increases, the likelihood and intensity of a possible reaction increases. Also, as the oxygen increases, there is more available to support combustion during the oxidation reaction with the system material(s).

i) Ignition energy in oxygen-rich environments can be derived from many sources. The heat of compression due to rapid pressure increases, the exothermic reaction resulting from the high rate of oxidation of some materials, or simply the available heat energy in the presence of low-ignition-temperature materials can cause items in oxygen-rich environments to ignite.

3.32.4 Affected Units or Equipment

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

b) Oxygen is sometimes used in SRUs (Figure 3-32-1 to Figure 3-32-3), FCC units, gasification units, and partial oxidation (POX) units.

c) Oxygen piping systems, especially valves, regulators, and other impingement areas, are potentially vulnerable. Non-metals such as those used for seats and seals are easier to ignite than metals. (Figure 3-32-6)

3.32.5 Appearance or Morphology of Damage

a) The worst situation is when the pressure envelope is breached because of fire. In that case, the appearance is obvious. Oxygen fires can cause significant burning of metal components and extensive structural damage. (Figure 3-32-4).

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

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

3.32.6 Prevention/Mitigation

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

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

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

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

d) Minimize lubricants and use only “oxygen-compatible” lubricants.

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

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

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

h) Avoid the use of plastic pipe in oxygen piping systems.

3.32.7 Inspection and Monitoring

a) Most commercial oxygen is dry and non-corrosive at normal ambient temperatures. Because of the sudden catastrophic ignition of metals under certain conditions, this type of damage cannot be inspected for in advance.

b) Tell-tale signs of a minor fire such as external heat damage or signs of malfunctioning valves or other components containing nonmetallic components may be indicative of a problem.

c) Blacklights can be used to check for hydrocarbon contamination.

3.32.8 Related Mechanisms

None.

3.32.9 References

1. CGA G-4.4, *Oxygen Pipeline and Piping Systems*, Compressed Gas Association, latest edition.

2. ASTM G88, *Standard Guide for Designing Systems for Oxygen Service*, American Society for Testing and Materials, West Conshohocken, PA.

3. ASTM G93, *Standard Practice for Cleaning Methods and Cleanliness Levels for Material and Equipment Used in Oxygen-enriched Environments*, American Society for Testing and Materials, West Conshohocken, PA.

4. CGA G-4.1, *Cleaning of Equipment for Oxygen Service*, Compressed Gas Association, latest edition.

5. NFPA 53M, *Fire Hazards in Oxygen-enriched Atmospheres*.

6. ASTM MNL36, *Safe Use of Oxygen and Oxygen Systems: Handbook for Design, Operation, and Maintenance*, Second Edition, H.D. Beeson, S.R. Smith, and W.F. Stewart, Editors, 2007.

7. ASTM G94, *Standard Guide for Evaluating Metals for Oxygen Service*, American Society for Testing and Materials, West Conshohocken, PA.

Figure 3-32-1—Thermal combustor on the front end of a reaction furnace on a SRU.

Figure 3-32-2—Same as figure above after damage due to oxygen combustion resulting from oxygen injection into the thermal combustor on the front end of the reaction furnace.

Figure 3-32-3—Same as figure above when viewed from a different angle.

Figure 3-32-4—Photograph of a burned 304 SS elbow. The fire started in an upstream stainless steel wire filter (due to particle impact), and the burning filter material impacted the elbow and ignited it. Thin stainless steel components (e.g. filter) are much more flammable than thicker stainless steel. Thin stainless steel (<$^1/_8$ in.) is usually avoided in oxygen systems.

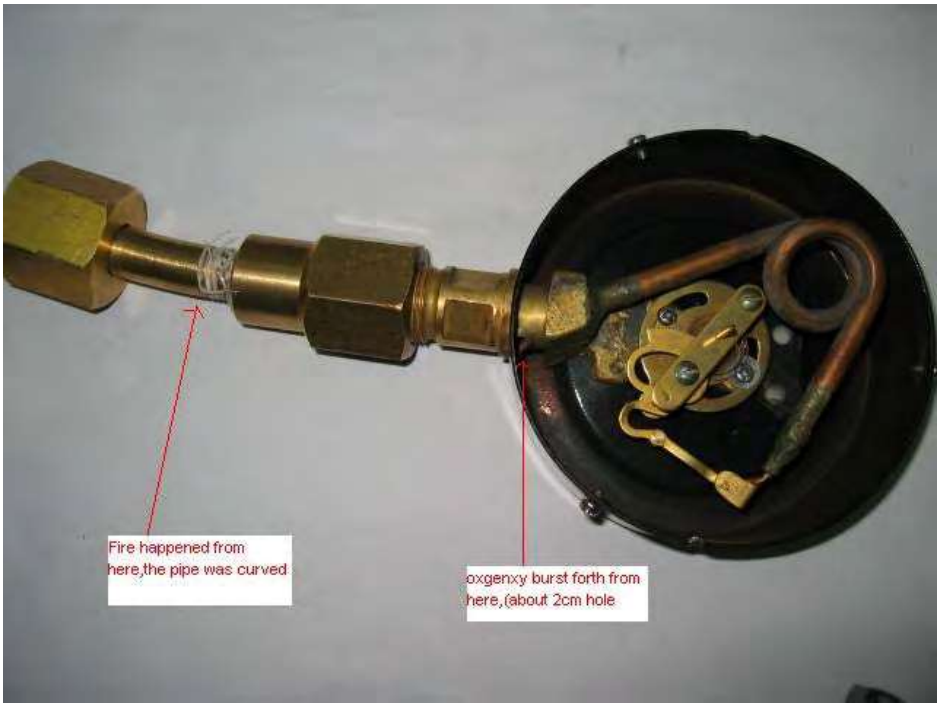


Figure 3-32-5—Photograph illustrating burn-through of a brass pressure gage. Brass is generally suitable for oxygen service. However, the gauge was not intended for oxygen service and was not "oil free." Hydrocarbon contamination, probably from manufacture, caused the fire.

Figure 3-32-6—Burn-through of a PTFE-lined stainless steel hose in high-pressure gaseous oxygen service. Grease contamination ignited and penetrated the hose.

3.33 Graphitic Corrosion of Cast Irons

3.33.1 Description of Damage

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

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

3.33.2 Affected Materials

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

3.33.3 Critical Factors

a) Graphitic corrosion is usually limited to very specific microstructure-environment combinations. Factors that influence graphitic corrosion include the composition of the cast iron and exposure conditions, including temperature, degree of aeration, pH, and exposure time. Damage increases with increasing temperature and aeration, and reduced pH.

b) Damage occurs in the presence of moisture or an aqueous phase, usually below 200 °F (95 °C).

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

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

e) Graphitic corrosion may accelerate corrosion of adjacent components by causing galvanic corrosion.

3.33.4 Affected Units or Equipment

Graphitic corrosion can occur in soft water, saltwater, mine waters, dilute acids, and in underground piping as well as in BFW equipment. Typical examples include feedwater piping, pumps [including pump impellers (Figure 3-33-1 and Figure 3-33-2)], valves, and underground cast iron pipe (Figure 3-33-3 and Figure 3-33-4). Fire-water systems are particularly vulnerable.

3.33.5 Appearance or Morphology of Damage

a) Graphitic corrosion normally turns cast iron charcoal gray. (Figure 3-33-2 and Figure 3-33-5)

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

c) The damage may not be noticeable upon VT even where the full wall thickness is degraded.

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

3.33.6 Prevention/Mitigation

a) It is often difficult to predict if exposure conditions will cause this form of dealloying in a particular environment or service. One must be aware of the potential susceptibility of cast irons.

b) Internal graphitic corrosion can be prevented by coatings and/or cement linings.

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

d) If practical, a material other than cast iron could be substituted.

3.33.7 Inspection and Monitoring

a) VT can be misleading as the metal surface will likely appear to be fine, other than some general surface corrosion or discoloration. VT cannot be used alone as a method of determining the presence of graphitic corrosion.

b) Affected surface areas are soft and can be carved away with a knife, course file, screwdriver, pencil, etc. However, this is not a definitive test and can only confirm the suspect area needs further investigation.

c) UT is not a good method to be used alone for detecting damage, but it has been reported to be able to locate the interface between sound metal and corroded metal.

d) Acoustic techniques (loss of "metallic ring") and ultrasonic attenuation may be applicable but are dependent upon the NDE technician's skill and equipment.

e) A significant reduction in hardness may accompany graphitic corrosion, although affected areas may be localized. Field hardness testing can separate sound metal from damaged areas and define the extent of the damaged area if it is not otherwise apparent.

    1. It may not be possible to get an actual hardness reading on severely damaged material. Rather, the brittle graphite might crack or crumble when attempting to test it. But this will clearly show that the material is affected.

f) Core sampling in thicker sections can be utilized to help gage the depth and occurrence.

g) Hammer testing (tapping) has been performed historically to determine the depth and extent of attack, but care must be taken because cast iron itself is brittle, and severely compromised material may fail completely. Also, hammer testing is inherently subjective.

h) Metallographic examination may be required to confirm the extent of damage. (Figure 3-33-6 to Figure 3-33-8)

3.33.8 Related Mechanisms

Dealloying (3.24). Graphitic corrosion is also known as selective leaching. It should not be confused with graphitization (3.34), the decomposition of carbides in steel at high temperatures.

3.33.9 References

1. R.D. Port and H.M. Herro, *The Nalco Guide to Boiler Failure Analysis*, McGraw-Hill, New York, NY, 1991, pp. 259–263.

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

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

4. *ASM Specialty Handbook—Cast Irons*, ASM International, Materials Park, OH, 1996.

5. M. Zamanzadeh, G. Kirkwood, S. Scheinman, and G. Bayer, "Corrosion Sensors for Detecting Graphitization of Cast Iron in Water Mains," Paper No. 07380, *Corrosion/2007*, NACE International, Houston, TX.

Figure 3-33-1—Graphitic corrosion of a cast iron pump impeller due to glycol acidification.

Figure 3-33-2—Cutaway of the cast iron impeller shown in Figure 3-32-1. The dark phase around the outside perimeter (at arrows) is graphite that surrounds the unaffected metal in the middle.

Figure 3-33-3—View of the outside of an underground concrete-lined saltwater service line that failed from graphitic corrosion.

Figure 3-33-4—View of concrete lining inside the failed line shown in Figure 3-32-3.

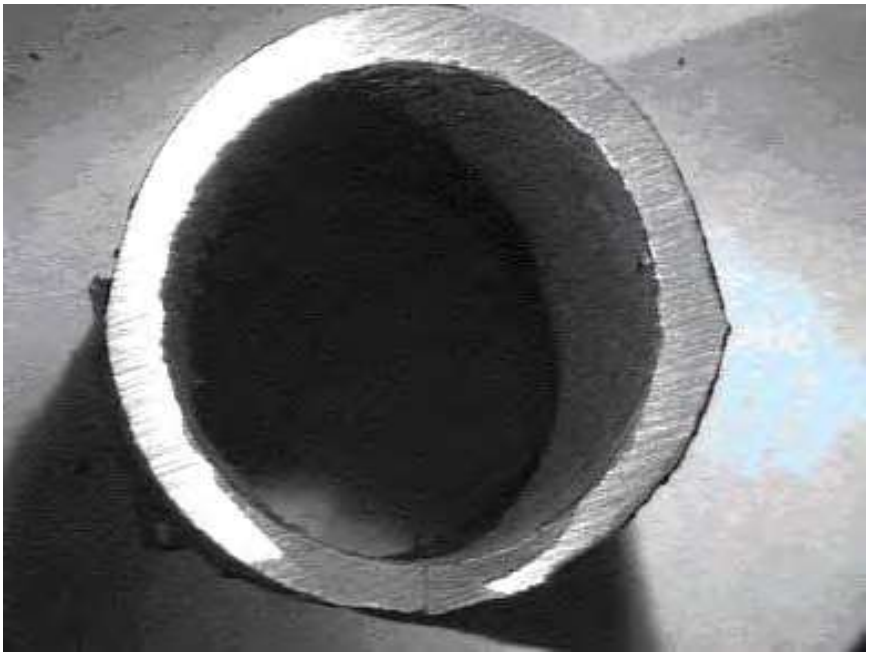


Figure 3-33-5—Cross section of a gray cast iron drainpipe showing charcoal colored thru-wall graphitic corrosion encroaching from both sides. Note the thru-wall crack at the bottom.

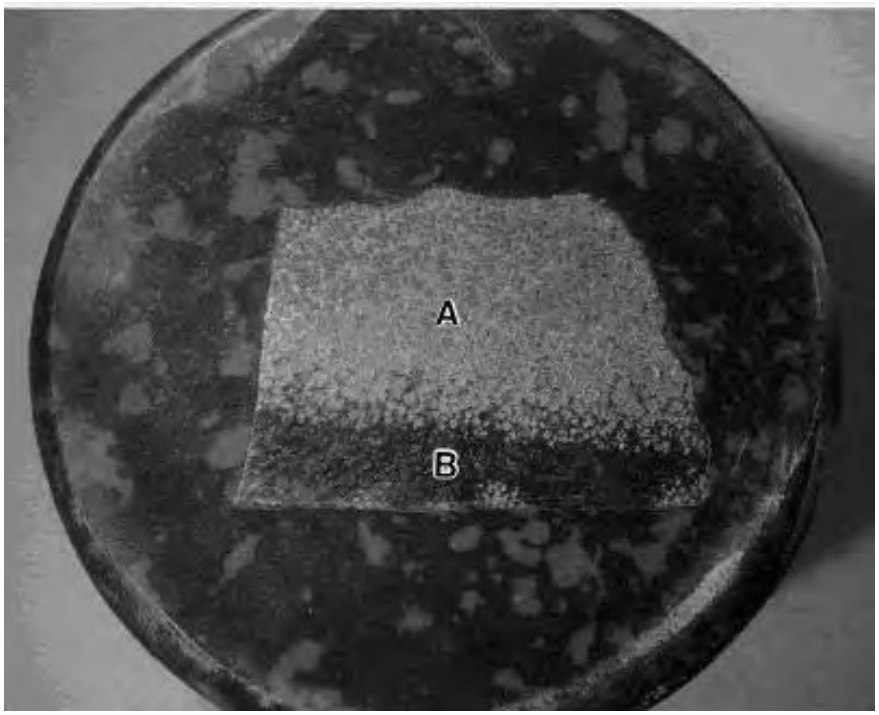


Figure 3-33-6—Cross section of a gray cast iron pipe with graphitic corrosion coming from the OD (Point B).

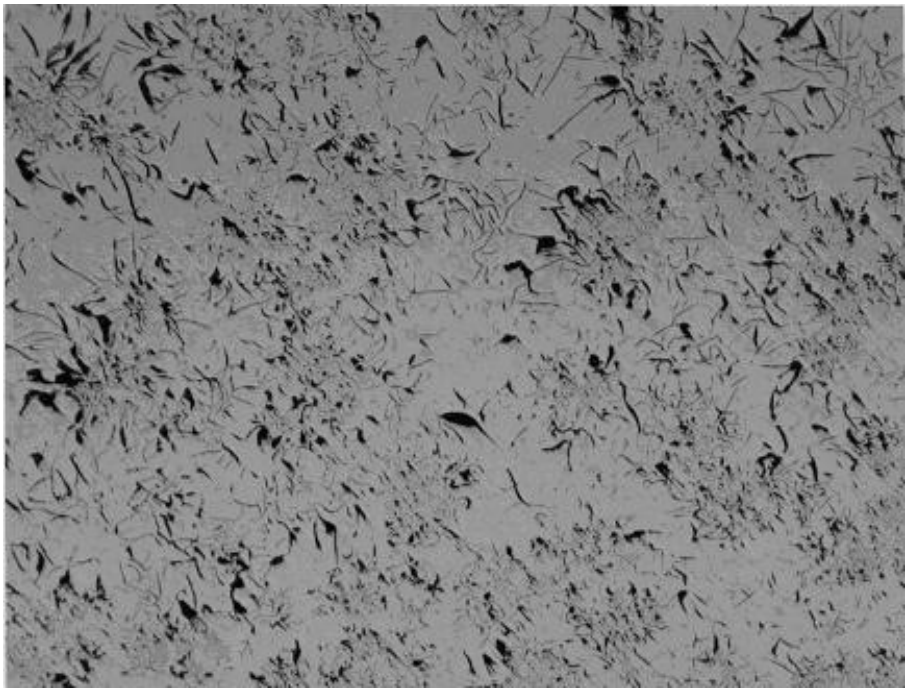


Figure 3-33-7—Higher-magnification view of unaffected area "A" shown in Figure 3-32-6.

Figure 3-33-8—Higher-magnification view of the damaged area "B" in Figure 3-32-6.

3.34 Graphitization

3.34.1 Description of Damage

Graphitization is a change in the microstructure of certain carbon steels and ½Mo steels after long-term operation in the 800 °F to 1100 °F (425 °C to 595 °C) range. At these temperatures, the carbide phases in these steels are unstable and decompose into graphite nodules. This decomposition of carbides may cause a loss in strength, ductility, and/or creep resistance.

3.34.2 Affected Materials

Some grades of carbon steel and ½Mo steels.

3.34.3 Critical Factors

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

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

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

d) Temperature has an important effect on the rate of graphitization. Below 800 °F (425 °C), the rate is extremely slow. The rate increases with increasing temperature.

e) There are two general types of graphitization.

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

2. The second and more damaging type of graphitization results in chains or local planes of concentrated graphite nodules. Because of its appearance, this type is also known as “eyebrow graphitization.” This form of graphitization can result in a significant reduction in load-bearing capability while increasing the potential for brittle fracture along this plane. There are two forms of this type of graphitization: (1) weld HAZ graphitization and (2) non-weld graphitization.

   — Weld HAZ graphitization is found adjacent to welds in a narrow band along the low-temperature edge of the HAZ. In multi-pass welded butt joints, these zones overlap each other. The graphite nodules that form at the low-temperature edge of these HAZs create a band of weak graphite extending through the entire cross section. (Figure 3-34-1 and Figure 3-34-2)

   — Non-weld graphitization is a form of localized graphitization that sometimes occurs along grain boundaries, constituent boundaries (between ferrite and pearlite), or planes of localized yielding in steels that have experienced significant plastic deformation as the result of cold working operations or bending. This type of graphitization also occurs in a chain-like manner.

f) The extent and degree of graphitization is usually reported in a qualitative fashion (none, slight, moderate, severe). Although it is difficult to predict the rate at which it forms, severe HAZ graphitization can develop in as little as 5 years at service temperatures above 1000 °F (540 °C). Very slight graphitization would be expected to be found after 30 to 40 years at 850 °F (455 °C). Time-temperature-transformation curves for HAZ graphitization can be found in Reference 2.

3.34.4 Affected Units or Equipment

a) Graphitization primarily occurs in carbon steel piping and hot-wall equipment in the FCC, catalytic reforming, and coker units.

b) Bainitic grades are less susceptible than coarse pearlitic grades.

c) Few failures directly attributable to graphitization have been reported in the refining industry. However, graphitization has been found where failure resulted primarily from other causes.

d) Several serious cases of graphitization have occurred in the reactors and piping of FCC units, as well as in carbon steel furnace tubes in a thermal cracking unit. Graphitization led to the failure of seal welds at the bottom tubesheet of a vertical waste heat boiler in an FCC. A graphitization failure was also reported in the long seam weld of a C-½Mo catalytic reformer reactor/interheater line.

e) Where concentrated eyebrow graphitization occurs along HAZs, the creep rupture strength may be drastically lowered. Slight to moderate amounts of graphite along the HAZs do not appear to significantly lower room-temperature or high-temperature properties.

f) Graphitization seldom occurs on boiling surface tubing in boilers but did occur in low-alloy C-½Mo tubes and headers during the 1940s. Economizer tubing, steam piping, and other related equipment that operates in the temperature range of 850 °F to 1025 °F (440 °C to 550 °C) are more likely to suffer graphitization.

3.34.5 Appearance or Morphology of Damage

a) Graphitization is not visible or readily apparent and can only be observed by metallographic examination. (Figure 3-34-2 to Figure 3-34-4)

b) At an advanced stage resulting in loss of creep strength, microvoids, microfissuring, subsurface cracking, or surface-connected cracking may be found.

3.34.6 Prevention/Mitigation

Graphitization can be prevented by using chromium containing low-alloy steels for long-term operation above 800 °F (425 °C).

3.34.7 Inspection and Monitoring

a) Evidence of graphitization is most effectively evaluated through removal of full-thickness samples for examination using metallographic techniques. Damage may occur mid-wall so that field replicas may be inadequate. Samples should be taken from areas where maximum temperature limits have been exceeded

b) Advanced stages of damage related to loss in strength include surface-breaking cracks or creep deformation that may be difficult to detect.

3.34.8 Related Mechanisms

Spheroidization (3.59) and graphitization are competing mechanisms that occur at overlapping temperature ranges. Spheroidization tends to occur preferentially above 1025 °F (550 °C), while graphitization predominates below this temperature.

3.34.9 References

1. H. Thielsch, *Defects and Failures in Pressure Vessels and Piping*, Rheinhold Publishing, New York, NY, 1965, pp. 49–83.

2. J.R. Foulds and R. Viswanathan, “Graphitization of Steels in Elevated-temperature Service,” *Proceedings of the First International Symposium: Microstructures and Mechanical Properties of Aging Materials*, November 1992.

3. R.D. Port, “Non-weld-related Graphitization Failures,” Paper No. 89248, *Corrosion/89*, NACE International, Houston, TX.

4. *ASM Handbook—Properties and Selection: Iron, Steels, and High-performance Alloys*, Volume 1, ASM International, Materials Park, OH.

5. D.N. French, “Microstructural Degradation,” The National Board of Boiler and Pressure Vessel Inspectors, http://www.nationalboard.com, June 2001.

6. J.G. Wilson, *Part 1: Graphitization of Steel in Petroleum Refining Equipment*, WRC Bulletin 032, Shaker Heights, OH, January 1957.

7. J.D. Dobis and L. Huang, “Assessment of Graphitized Carbon Steel Tubes in Fired Heater Service,” Paper No. 05559, *Corrosion/2005*, NACE International, Houston, TX.

8. *Review of the Existing Technology for the Detection of Graphitization Damage in Carbon and Carbon-Molybdenum Steel Piping and Tubing*, EPRI, Product ID: 3002003421, July 2, 2014.

9. H.J. Kerr and F. Eberle, “Graphitization of Low-carbon and Low-carbon-molybdenum Steels,” Welding Research Supplement, February 1945.

10. J. Hau et al., “Evaluation of Aging Equipment for Continued Service,” Paper No. 05558, *Corrosion/2005*, NACE International, Houston, TX.

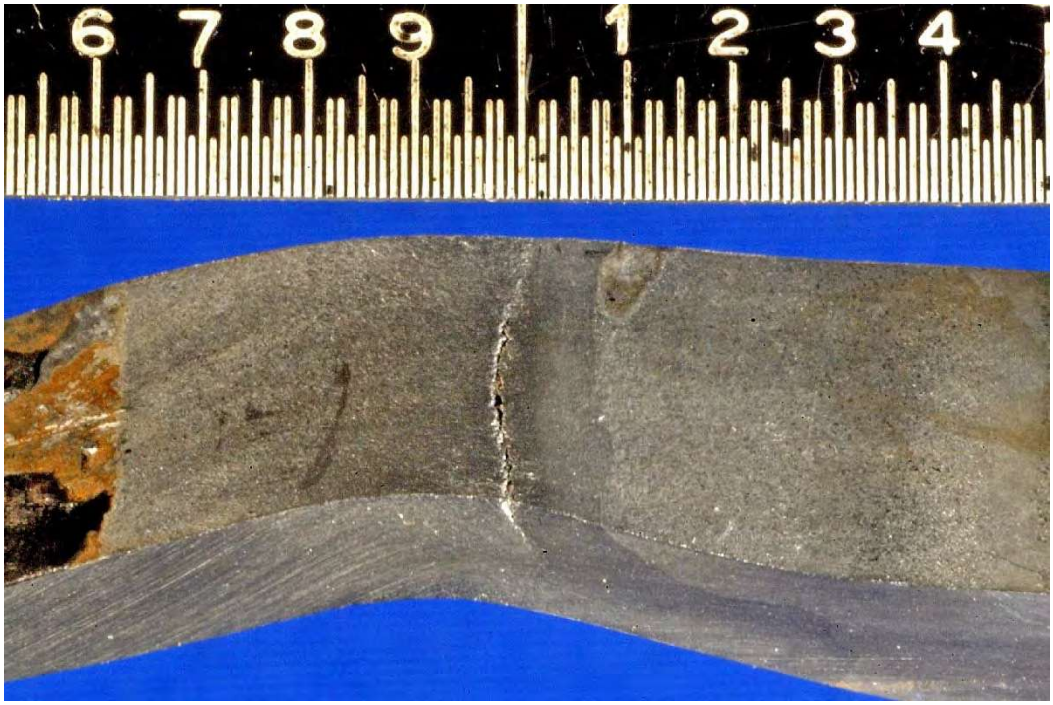


Figure 3-34-1—A crack opened up along the low-temperature edge of the HAZ when a graphitized piece of steel was subjected to a bending test. The scale in the photo is in tenths of an inch. (Reference 10)

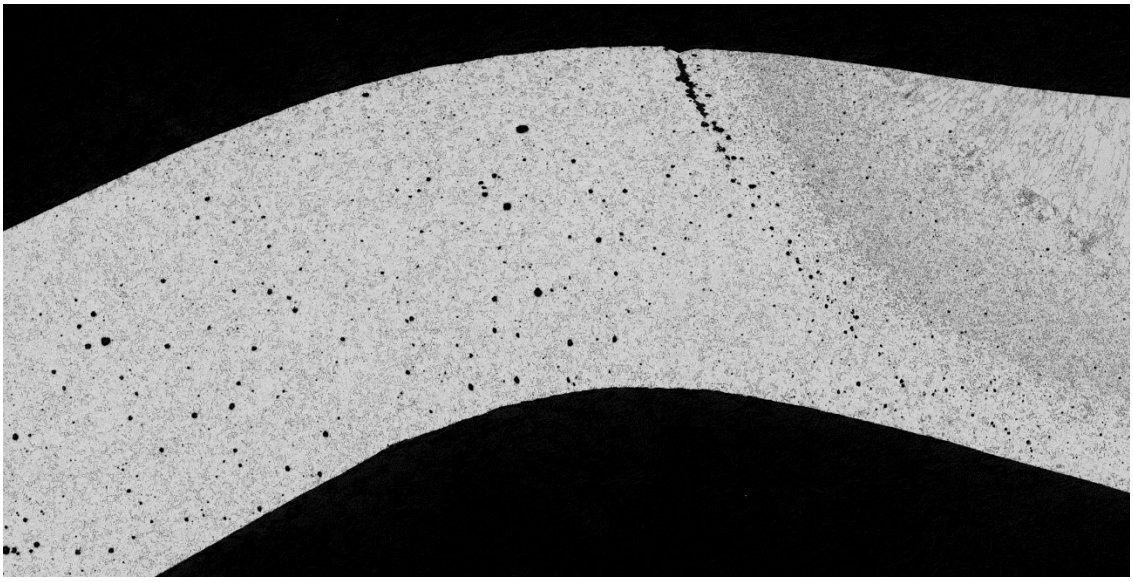


Figure 3-34-2—A polished and etched side view of the sample in Figure 3-33-1 shows aligned graphitization along the low-temperature edge of the HAZ as well as random graphitization in the base metal. (Reference 10)

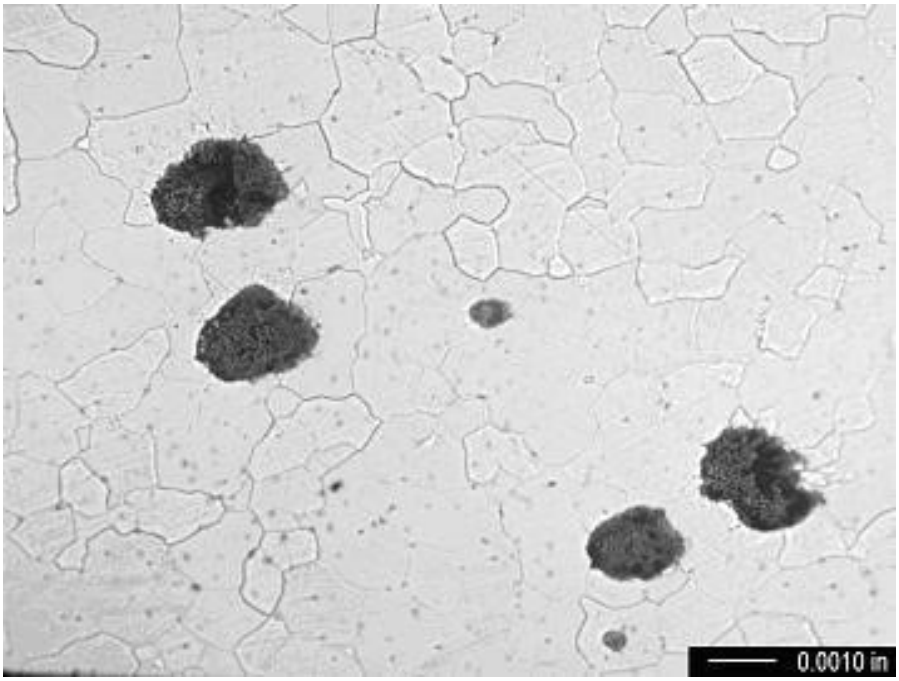


Figure 3-34-3—High-magnification photomicrograph of a metallographic sample showing graphite nodules. Compare to normal microstructure shown in Figure 3-33-4.

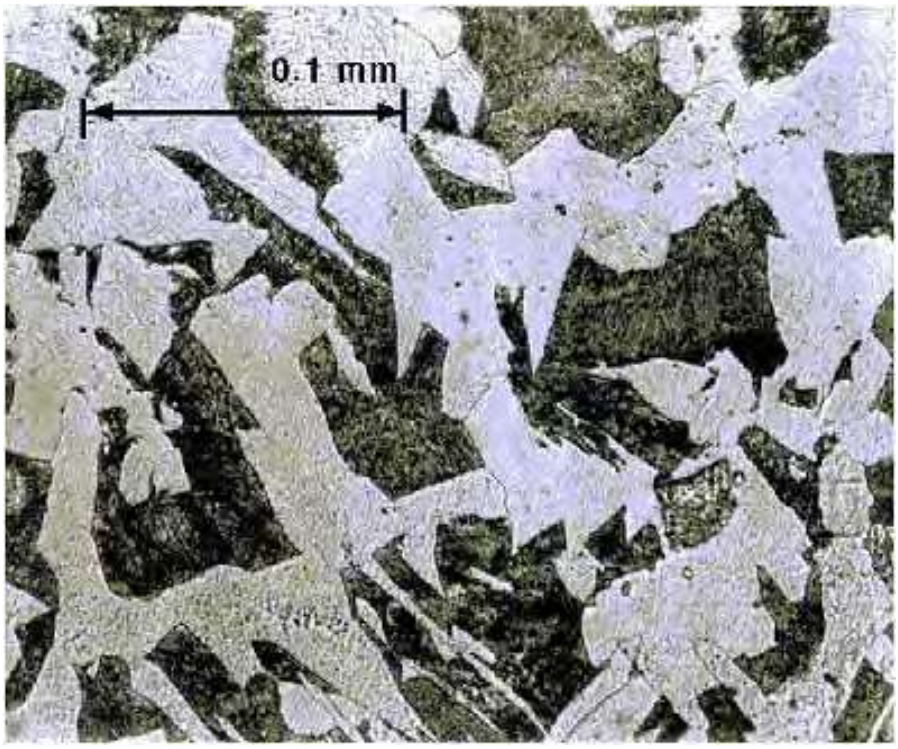


Figure 3-34-4—High-magnification photomicrograph of metallographic sample showing typical ferrite-pearlite structure of carbon steel.

3.35 High-temperature H_2/H_2S Corrosion

3.35.1 Description of Damage

The presence of hydrogen in H_2S-containing hydrocarbon streams increases the severity of high-temperature sulfidation (sulfidic) corrosion at temperatures above about 450 °F (230 °C). Because of the smooth, large, relatively uniformly corroded surface produced by high-temperature H_2/H_2S corrosion, it can lead to rupture-type failure rather than a localized or pinhole leak. This subject is covered in much greater detail in Reference 3 (API 939-C).

3.35.2 Affected Materials

For the materials typically used in this service, the order of increasing resistance is carbon steel, low-alloy steels, 400 series SS, and 300 series SS. However, for a practical, useful improvement over carbon steel, the alloy content of at least 9Cr-1Mo is normally needed.

3.35.3 Critical Factors

a) The critical factors for high-temperature H_2/H_2S corrosion are the temperature, the presence of hydrogen, the concentration and partial pressure of H_2S, the vapor/liquid ratio, and the chemical composition of the alloy.

b) Depending on the quantity of hydrogen present, corrosion rates may be significantly different than those associated with high-temperature sulfidation in the absence of hydrogen. (See 3.61.)

c) Sulfidation rates increase with increasing H_2S content and especially increasing temperature. Figure 3-35-1 shows the effect of temperature and H_2S content on the corrosion rate of carbon steel.

d) Increasing chromium content of the alloy improves resistance. However, there is little improvement with increasing chromium content until about 7 % to 9 % Cr as shown by the relative rate reduction factors in Table 3-35-1. The benefit of higher chromium levels is shown in Figure 3-35-2.

e) Chromium-containing nickel-based alloys have resistance similar to stainless steel. Similar levels of chromium provide similar corrosion resistance.

f) Primarily due to the higher partial pressure of H_2S, corrosion rates in higher-pressure units, e.g. hydrocrackers and gas oil hydrotreaters (desulfurizers), are generally higher than those in lower-pressure naphtha hydrotreaters.

3.35.4 Affected Units or Equipment

a) This form of corrosion occurs in piping and equipment in units where high-temperature H_2/H_2S streams are found, which is primarily hydroprocessing units (hydrotreaters and hydrocrackers).

b) Noticeable increases in corrosion rates may be found downstream of the hydrogen injection point where the mechanism changes from sulfidation (3.61) to high-temperature H_2/H_2S corrosion. The addition of hydrogen promotes cracking of the reactive sulfur species into H_2S prior to the reactor, increasing the rate of corrosion in comparison to corrosion from the reactive sulfur alone.

3.35.5 Appearance or Morphology of Damage

a) Corrosion will appear as a uniform loss in thickness from the process side and is accompanied by the formation of an iron sulfide scale.

b) Scale is about five times the volume of lost metal and may be in multiple layers.

c) The tightly adherent shiny gray scale attached to the surface may be mistaken for unaffected metal.

3.35.6 Prevention/Mitigation

a) The corrosion damage is minimized by using alloys with sufficiently high chromium content.

b) The 300 series SS such as Types 304L, 316L, 321, and 347 are highly resistant at typical service temperatures.

c) Aluminum diffusion treatment is sometimes used to reduce corrosion rates and prolong the life of thin components such as 300 series SS catalyst support screens in hydroprocessing reactors.

d) Process simulations should be checked periodically to confirm that H_2S levels have not significantly increased.

3.35.7 Inspection and Monitoring

a) Thinning in piping and tubing can be detected and measured using UT thickness measurement or RT. Thinning in pressure vessels can be detected by internal VT and measured 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 a more thorough examination and may find thinning missed by spot UT testing.

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.

3.35.8 Related Mechanisms

High-temperature sulfidation in the absence of hydrogen is discussed in 3.61.

3.35.9 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.

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

3. API Recommended Practice 939-C, *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries*, American Petroleum Institute, Washington, DC.

Table 3-35-1—Rate Factors vs Chromium Content (Reference 2)

Alloy	Rate Factor
CS, C-0.5Mo	1
1Cr-0.5Mo	0.96
2.25Cr-1Mo	0.91
5Cr-0.5Mo	0.80
7Cr-1Mo	0.74
9Cr-1Mo	0.68

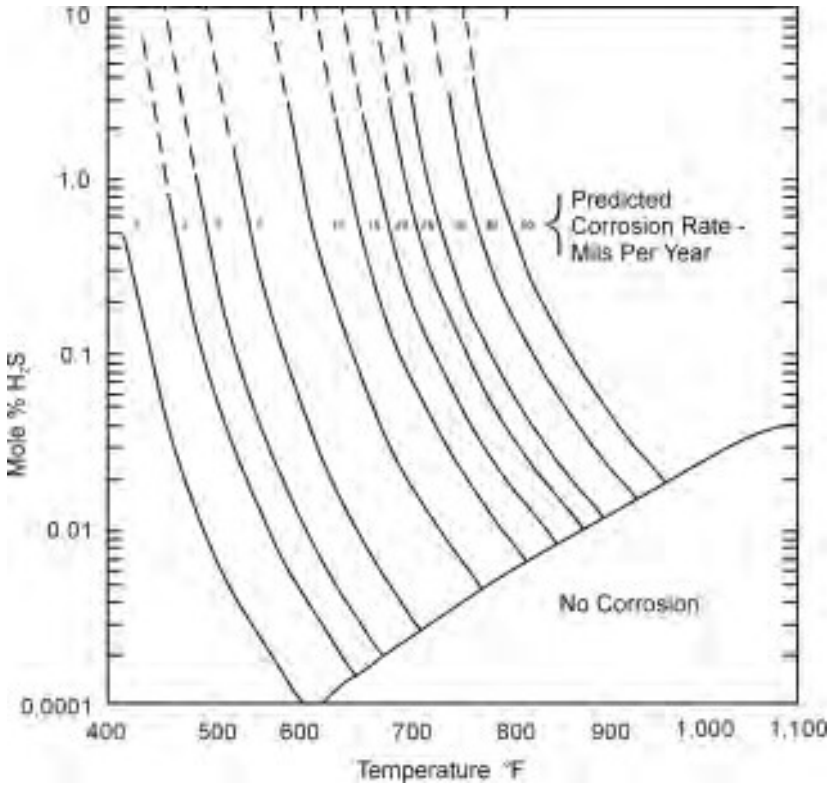


Figure 3-35-1—Corrosion rate of carbon steel in H_2/H_2S service in a naphtha desulfurizer from the modified Couper-Gorman curves. (Reference 1)

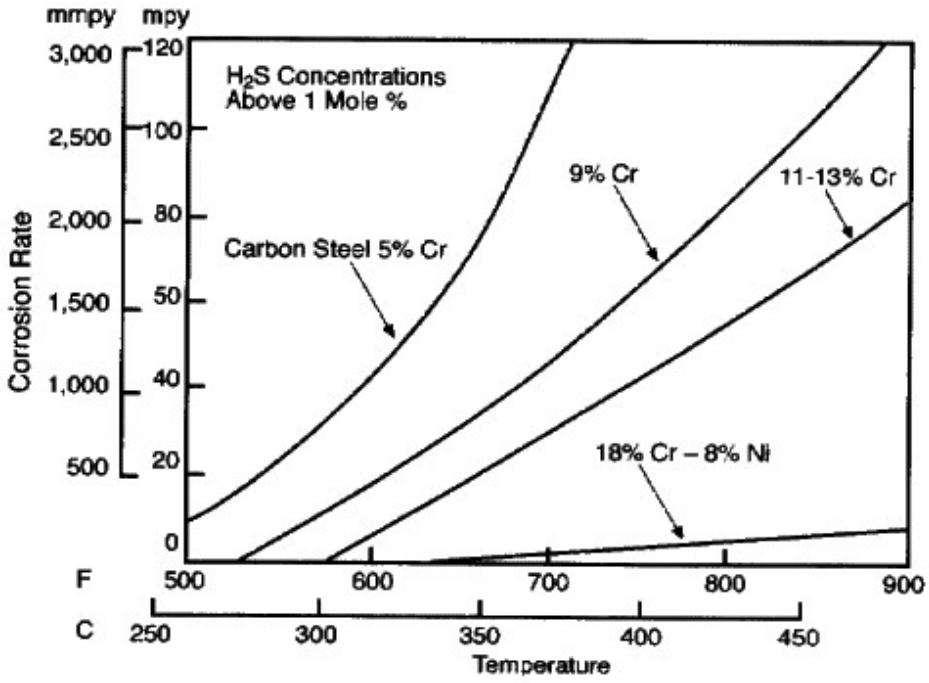


Figure 3-35-2—Corrosion rate curves for Cr-containing alloys in H_2/H_2S service. (Reference 1)

3.36 High-temperature Hydrogen Attack

3.36.1 Description of Damage

a) High-temperature hydrogen attack (HTHA) results from exposure of steels to hydrogen gas at elevated temperatures and pressures. Dissociated hydrogen atoms react with carbon and carbides in the steel to form CH_4.

b) The hydrogen/carbon reaction can cause surface decarburization of the steel. Surface decarburization alone is normally not detrimental to the point of limiting the life of equipment but may be indicative of internal HTHA. Extensive decarburization will reduce component strength. (See 3.25 for more on decarburization.)

c) If diffusion of carbon to the surface is limited, CH_4 is formed internally from internal decarburization. Internal CH_4 cannot diffuse through the steel. As a result, internal CH_4 pressure builds up, initially forming bubbles or cavities, then microfissures, and finally fissures that may combine to form cracks. Internal damage leading to cracking is the more serious effect of HTHA, and it can lead to equipment failure.

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

e) Blistering may also occur due to either molecular hydrogen (from re-combined hydrogen atoms) or CH_4 accumulating in laminations or other conducive sites in the steel.

f) See Reference 1 (API RP 941) for more detailed information on HTHA.

3.36.2 Affected Materials

a) In order of increasing resistance: as-welded (non-PWHT) carbon steel, non-welded carbon steel and carbon steel that has received PWHT, C-0.5Mo, Mn-0.5Mo, 1Cr-0.5Mo, 1.25Cr-0.5Mo, 2.25Cr-1Mo, 2.25Cr-1Mo-V, 3Cr-1Mo, 5Cr-0.5Mo, and similar steels with variations in chemistry.

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

3.36.3 Critical Factors

a) Resistance to HTHA increases with an increase in the alloy content, primarily the Cr and Mo content, of a steel. For a specific material, HTHA is dependent on temperature, hydrogen partial pressure, time, and stress level.

b) Figure 3-36-1, from API RP 941, is a set of curves that show the combined temperature and hydrogen partial pressure safe operating limits for carbon steel and low-alloy steels. Operation at a temperature and H_2 partial pressure below the curve for a particular material is considered safe. Operation above the curve indicates susceptibility to HTHA. Additional information on HTHA can be found in API RP 941.

c) HTHA damage is preceded by a period of time when no noticeable change in properties is detectable by normal mechanical testing techniques nor is any internal damage detectable with any NDE methods. This period of time is called the incubation period.

    1. During the incubation period, the amount of internal damage (cavity and microfissure formation and growth) increases to the point where it can be detected and measured with available inspection techniques. It may vary from hours under very severe conditions to many years.

d) The damage is irreversible, and service exposure time is cumulative. After the incubation period, the amount of damage continues to increase during the time the material is exposed to damaging temperature and H_2 partial pressure conditions, whether the exposure is continuous or periodic.

e) Applied or residual tensile stress can increase the rate of HTHA damage occurring in a susceptible material. Stress-relieving carbon steel welds by PWHT is known to reduce susceptibility to HTHA.

3.36.4 Affected Units

a) Hydroprocessing units such as hydrotreaters (desulfurizers) and hydrocrackers, catalytic reformers, some ISOM units, hydrogen manufacturing units, and hydrogen cleanup units such as pressure swing absorption units all have equipment operating under conditions where HTHA can occur in a susceptible material.

b) Boiler tubes in very high pressure steam service can also suffer HTHA.

3.36.5 Appearance or Morphology of Damage

a) The location within a piece of equipment where HTHA will occur is generally unpredictable. HTHA that led to equipment failure or replacement has occurred in weld HAZs as well as base metal away from welds. It is less commonly found in weld metal.

b) HTHA can be confirmed through the use of specialized techniques including metallographic and SEM analysis of damaged areas. (Figure 3-36-2 to Figure 3-36-6)

c) The steel surface may be decarburized. (Figure 3-36-4)

d) Internal decarburization can lead to internal fissuring and cracking, which in the later stages of damage can be seen using standard metallography. (Figure 3-36-5 to Figure 3-36-6)

e) In the earliest stages of HTHA, bubbles/cavities in samples can be detected by SEM, although it may be difficult to tell the difference between HTHA cavities and creep cavities. (Some refinery services expose low-alloy steels to both HTHA and creep conditions.) Advanced metallographic analysis of damaged areas can detect the early stages of microfissuring.

f) Cracking and fissuring are intergranular and occur adjacent to pearlite (layers of ferrite and iron carbide) areas in carbon steels.

g) Cracking along the HAZ and fusion line can occur in carbon steel as the result of highly localized HTHA, with adjacent areas exhibiting little or no fissuring or decarburization

h) Blistering may be visible to the naked eye.

3.36.6 Prevention/Mitigation

a) Using alloy steels with chromium and molybdenum will increase carbide stability, thereby minimizing CH_4 formation and resistance to HTHA. Other carbide stabilizing elements include tungsten and vanadium.

b) Common design practice is to use a 25 °F to 50 °F (15 °C to 30 °C) and 25 psia to 50 psia (170 KPa to 345 KPa) hydrogen partial pressure safety factor approach when using the API RP 941 curves.

c) The API RP 941 curves, with the current version shown in Figure 3-36-1, have been revised several times since they were first introduced.

1. The C-½Mo curve was removed from Figure 3-36-1 in 1990 because of a number of cases of HTHA in C-½Mo steels in refinery service under conditions that were previously considered safe, i.e. below the previously existing C-½Mo curve. This material is not recommended for new construction in hot hydrogen services. (C-½Mo carbide stability under HTHA conditions is variable due to the different carbides formed during the various heat treatments applied to fabricated equipment.)

d) For existing C-½Mo equipment, the concern about its unpredictable resistance to HTHA has prompted refiners to perform reviews of inspection effectiveness and cost vs replacement with a more suitable alloy.

1. Non-stress-relieved carbon steel welds have also shown a higher susceptibility to HTHA compared to stress-relieved welds and non-welded components. In response, the Eighth Edition of API RP 941 added a new, lower curve for carbon steel welded with no PWHT, as shown in Figure 3-36-1.

e) 300 series SS weld overlay and roll bond cladding, and in some cases 400 series SS cladding, are typically used in high-temperature hydrogen service where the base metal does not have adequate high-temperature H_2/H_2S corrosion resistance. Properly metallurgically bonded stainless steel overlay or cladding will decrease the hydrogen partial pressure seen by the underlying base metal; however, most refiners do not take credit for this in the design of new equipment. New equipment should be designed so the base material is inherently resistant to HTHA under expected service conditions without taking into account any added HTHA resistance provided by the weld overlay or cladding.

1. In some cases, refiners take the decrease in effective partial pressure into account when evaluating the risk of HTHA in existing equipment.

3.36.7 Inspection and Monitoring

a) Damage may occur randomly in the base metal, weld HAZs, and occasionally in welds.

b) HTHA can occur in the base metal at locations remote from welds. In vessels with internal cladding or weld overlay, HTHA damage can occur in the base metal at locations where the cladding or weld overlay has cracked and become disbonded, especially if credit was taken for the cladding reducing the effective H_2 partial pressure at the base metal, i.e. where the vessel's operating conditions exceeded the API RP 941 curve for unprotected base metal. PT of the cladding or weld overlay for cracking can assist in identifying areas that may have HTHA damage in the base metal underneath the cracked cladding or weld overlay.

1. VT for bulging of the cladding or weld overlay away from the underlying base metal may also aid in identifying suspect areas of HTHA damage in the base metal.

2. Localized damage under cladding or weld overlay might be overlooked if inspection methods focus only on the weld seams and nozzles. (Reference 4)

c) While FMR can detect microvoids, fissures, and decarburization, it is best suited for examination in areas of known HTHA damage and is generally not relied upon as the primary tool for damage detection. Most equipment has decarburized surfaces due to the various heat treatments used during fabrication, and microvoids and fissures may also be absent on the surface. Experience has shown that removal of metal up to 0.1 in. (2 mm) may be needed for finding HTHA damage.

d) VT for blisters on the inside surface may indicate CH_4 formation and potential HTHA. However, HTHA mostly occurs without the formation of surface blisters.

e) The use of NDE methods to detect internal HTHA requires highly specialized training, skills, and experience. It has had mixed results and is an area of ongoing development. As of this writing, the NDE table in API RP 941 is undergoing revision.

1. Automated ultrasonic backscatter testing (AUBT) and angle beam spectral analysis (ABSA) have had some success finding fissuring, i.e. where microvoids and microfissures have grown to form significant fissures in the base metal as well as in welds and HAZs, but it can also miss significant cracking and is not considered reliable.

2. TOFD and PAUT have shown promise in finding surface-connected and internal damage.

3. Conventional NDE methods for crack detection, e.g. WFMT, PT, or MT, are generally not useful for HTHA inspection except where gross cracking has occurred and reached the metal surface.

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

5. Ultrasonic attenuation and velocity ratio have been found to be unreliable techniques for HTHA detection and should not be used as primary inspection methods.

3.36.8 Related Mechanisms

Decarburization (3.25). A form of HTHA can occur in boiler tubes and is referred to by the fossil utility industry as hydrogen damage.

3.36.9 References

1. API Recommended Practice 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*, 8th Edition, American Petroleum Institute, Washington, DC

2. F.H. Vitovec et al., "The Growth Rate of Fissures During Hydrogen Attack of Steels," *Proceedings of the API Division of Refining*, Vol. 44, No. 3, 1964, pp. 179–188.

3. "Fitness-For-Service Evaluation Procedures for Operating Pressure Vessels, Tanks, and Piping in Refinery and Chemical Service," Materials Properties Council, FS-26, Draft No. 5, Consultants Report, NY, 1995.

4. S. Decker et al., "Safe Operation of a High Temperature Hydrogen Attack Affected DHT Reactor," Paper No. 09339, *Corrosion/2009*, NACE International, Houston, TX.

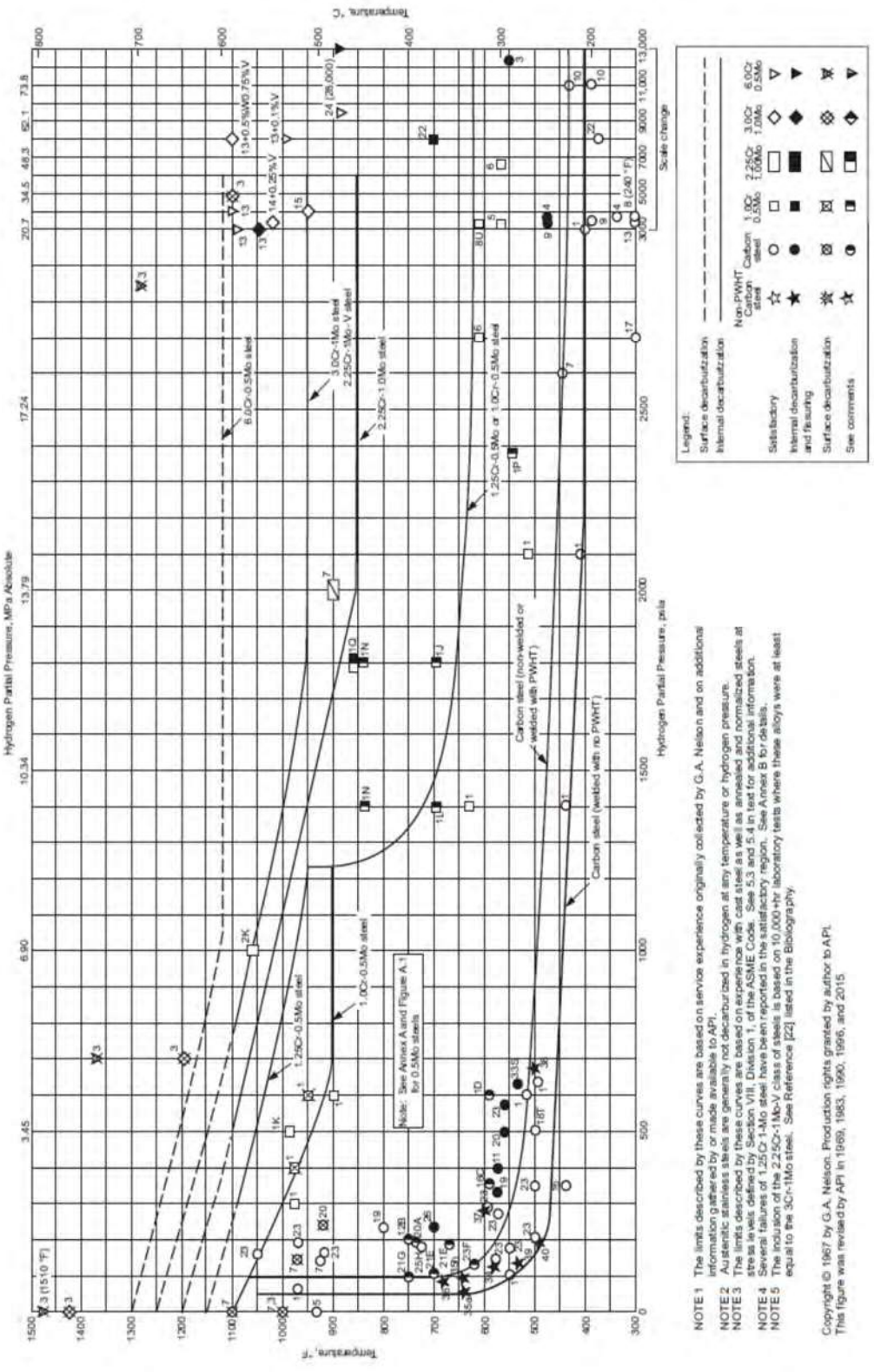


Figure 3-36-1—Recommended temperature and H_2 partial pressure limits per API RP 941. (Reference 1)