

Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants

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Introduction

At normal atmospheric temperatures, gaseous molecular hydrogen does not readily permeate steel, even at high pressures. Carbon steel is the standard material for cylinders that are used to transport hydrogen at pressures of 2000 psi (14 MPa). Many postweld heat treated carbon steel pressure vessels have been used successfully in continuous service at pressures up to 10,000 psi (69 MPa) and temperatures up to 430 °F (221 °C). However, under these same conditions, highly stressed carbon steels and hardened steels have cracked due to hydrogen embrittlement.

The recommended maximum hydrogen partial pressure at atmospheric temperature for carbon steel fabricated in accordance with the ASME *Boiler and Pressure Vessel Code* is 13,000 psia (90 MPa). Below this pressure, carbon steel equipment has shown satisfactory performance. Above this pressure, very little operating and experimental data are available. If plants are to operate at hydrogen partial pressures that exceed 13,000 psia (90 MPa), the use of an austenitic stainless steel liner with venting in the shell should be considered.

At elevated temperatures, molecular hydrogen dissociates into the atomic form, which can readily enter and diffuse through the steel. Under these conditions, the diffusion of hydrogen in steel is more rapid. As discussed in Section 4, hydrogen reacts with the carbon in the steel to cause either surface decarburization or internal decarburization and fissuring, and eventual cracking. This form of hydrogen damage is called high temperature hydrogen attack (HTHA), and this recommended practice discusses the resistance of steels to HTHA.

Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants

1 Scope

This recommended practice (RP) summarizes the results of experimental tests and actual data acquired from operating plants to establish practical operating limits for carbon and low alloy steels in hydrogen service at elevated temperatures and pressures. The effects on the resistance of steels to hydrogen at elevated temperature and pressure that result from high stress, heat treatment, chemical composition, and cladding are discussed. This RP does not address the resistance of steels to hydrogen at lower temperatures [below about 400 °F (204 °C)], where atomic hydrogen enters the steel as a result of an electrochemical mechanism.

This RP applies to equipment in refineries, petrochemical facilities, and chemical facilities in which hydrogen or hydrogen-containing fluids are processed at elevated temperature and pressure. The guidelines in this RP can also be applied to hydrogenation plants such as those that manufacture ammonia, methanol, edible oils, and higher alcohols.

The steels discussed in this RP resist high temperature hydrogen attack (HTHA) when operated within the guidelines given. However, they may not be resistant to other corrosives present in a process stream or to other metallurgical damage mechanisms that can occur in the operating HTHA range. This RP also does not address the issues surrounding possible damage from rapid cooling of the metal after it has been in high temperature, high pressure hydrogen service (e.g. possible need for outgassing hydroprocessing reactors). This RP discusses in detail only the resistance of steels to HTHA.

Presented in this document are curves that indicate the operating limits of temperature and hydrogen partial pressure for satisfactory resistance of carbon steel and Cr-Mo steels to HTHA in elevated temperature hydrogen service. In addition, it includes a summary of inspection methods to evaluate equipment for the existence of HTHA.

2 Normative References

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For undated references, the latest edition of the referenced document (including any addenda) applies.

API 510, *Pressure Vessel Inspection Code: In-Service Inspection, Rating, Repair, and Alteration*

API 570, *Piping Inspection Code: In-Service Inspection, Rating, Repair, and Alteration of Piping Systems*

API Recommended Practice 584, *Integrity Operating Windows*

ASME Boiler and Pressure Vessel Code (BPVC) ¹, Section VIII: Pressure Vessels; Division 1

ASME Boiler and Pressure Vessel Code (BPVC), Section VIII: Pressure Vessels; Division 2

ASME/ANSI ² Code for Pressure Piping B31.3, *Chemical Plant and Petroleum Refinery Piping*

AWS D10.10/D10.10M ³, *Recommended Practices for Local Heating of Welds in Piping and Tubing*

WRC Bul-452 ⁴, *Recommended Practices for Local Heating of Welds in Pressure Vessels*

¹ ASME International, 2 Park Avenue, New York, New York 10016-5990, www.asme.org.

² American National Standards Institute, 25 West 43rd Street, 4th Floor, New York, New York 10036, www.ansi.org.

³ American Welding Society, 8669 NW 36 Street, # 130, Miami, Florida 33166-6672, www.aws.org

⁴ Welding Research Council, P.O. Box 201547, Shaker Heights, Ohio 44122, www.forengineers.org

3 Operating Experience

3.1 Basis for Setting Integrity Operating Windows

Figure 1 illustrates the resistance of steels to attack by hydrogen at elevated temperatures and hydrogen pressures. HTHA of steel can result in surface decarburization, internal decarburization, fissuring, and cracking, or a combination of these (see Section 4). Figure 1 gives the operating conditions (process temperature and hydrogen partial pressure) above which these types of damage can occur.

Figure 1 is based upon experience gathered since the 1940s. Supporting data were obtained from a variety of commercial processes and laboratory experiments (see the References to Figure 1). While temperature and hydrogen partial pressure data were not always known precisely, the accuracy is often sufficient for commercial use. Satisfactory performance has been plotted only for samples or equipment exposed for at least 1 year. Unsatisfactory performance from laboratory or plant data has been plotted, regardless of the length of exposure time. The chemical compositions of the steels in Figure 1 should conform to the limits specified for the various grades by ASTM/ASME.

Owners/operators should develop integrity operating windows (IOWs) (as outlined in API 584) to manage risks associated with HTHA by using operational experience presented in this document.

Since the original version of Figure 1 was prepared for API in 1949 [1], further experience has enabled curves for most commonly used steels to be more accurately located. All information relevant to 0.5Mo steels (C-0.5Mo and Mn-0.5Mo) is summarized in Annex A.

The Fifth Edition of this RP also added three data points, which show HTHA of 1.25Cr-0.5Mo steel below the current 1.25Cr-0.5Mo curve. See Annex B for more discussion of 1.25Cr-0.5Mo steel. Annex C gives a similar discussion for 2.25Cr-1.0Mo steel.

This Eighth Edition adds 12 data points and a new curve labeled as “Carbon steel (welded with no PWHT)” for HTHA of carbon steel not subjected to postweld heat treatment (PWHT), which is below the carbon steel curve appearing in all previous editions and now labeled as “Carbon steel (non-welded or welded with PWHT).” See Annex F for more discussion on carbon steel welds not subjected to PWHT.

3.2 Selecting Materials for New Equipment

The API Subcommittee on Corrosion and Materials collects data on the alloys shown in all figures or similar alloys that may come into use. Follow the guidance in Annex H for submitting new data.

Figure 1 is often used when selecting materials for new equipment in hydrogen service. When using Figure 1 as an aid for materials selection, it is important to recognize that Figure 1 only addresses a material's resistance to HTHA. It does not take into account other factors important at high temperatures such as:

- a) other corrosive species that may be in the system such as hydrogen sulfide;
- b) creep, temper embrittlement, or other high temperature damage mechanisms;
- c) interaction of hydrogen and stress (primary, secondary, and residual); and
- d) synergistic effects such as between HTHA and creep.

Temperatures for data plotted in the figures represent a range in operating conditions that in previous editions was stated to be about ± 20 °F (± 11 °C). Because of the uncertainty of the actual operating conditions over many decades of operation for data points contained in the curves, users need to understand that Figure 1 is based largely upon empirical experience and from the guidance in API TR 941 [39]. Therefore, an operating company should add a safety margin, below the relevant curve, when selecting steels.

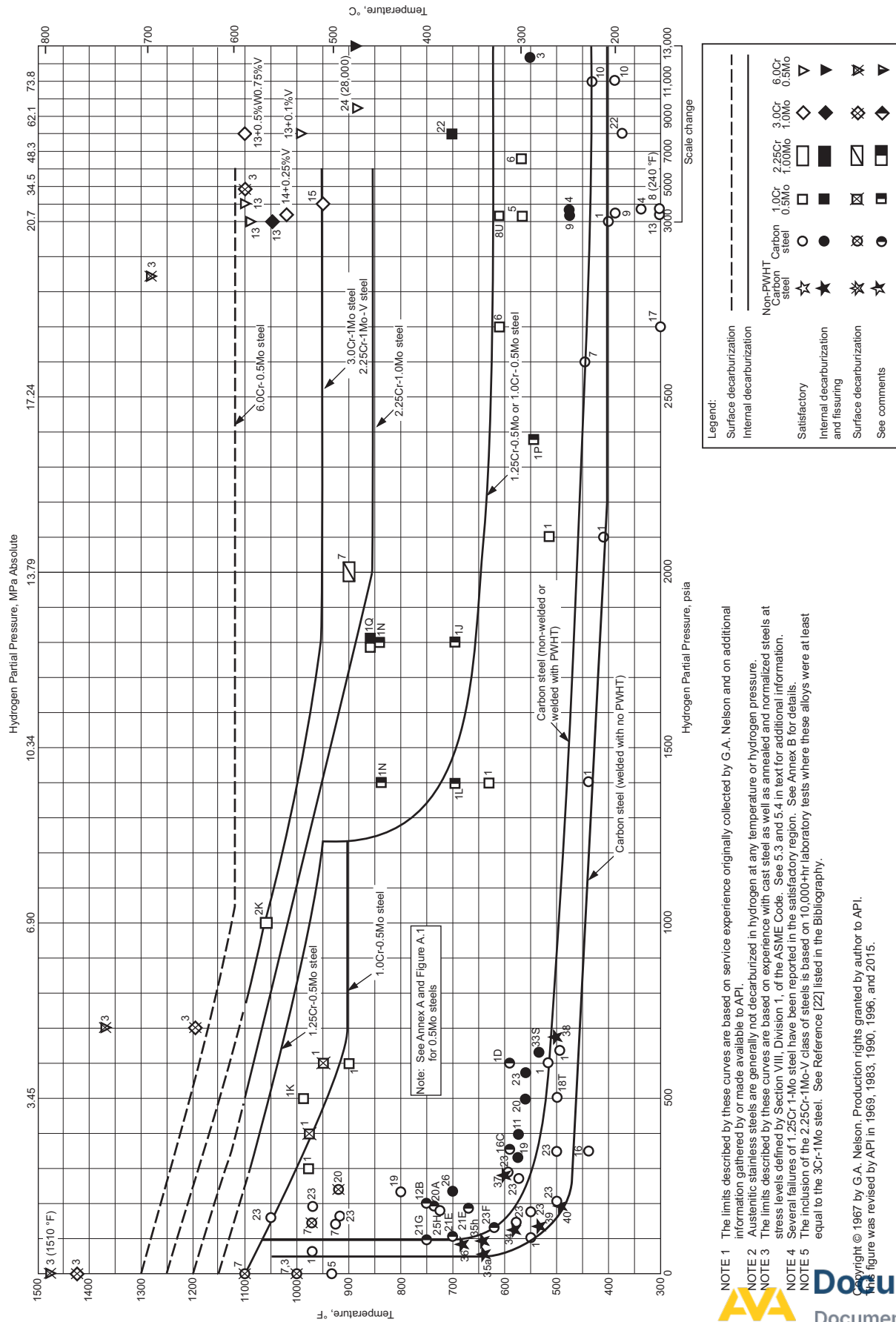


Figure 1—Operating Limits for Steels in Hydrogen Service to Avoid High Temperature Hydrogen Attack

3.3 High Temperature Hydrogen Attack (HTHA) in a Liquid Hydrocarbon Phase

HTHA can occur in a liquid hydrocarbon phase if it can occur in the gas phase in equilibrium with the liquid phase. For materials selection purposes (using Figure 1), hydrogen dissolved in liquid hydrocarbon should be assumed to exert a vapor pressure equal to the hydrogen partial pressure of the gas with which the liquid is, or was last, in equilibrium. Recent plant experience and testing of field-exposed specimens have shown that HTHA can occur under such conditions [10].

HTHA has been found in liquid-filled carbon steel piping downstream of a heavy oil desulfurization unit separator that was operating at hydrogen partial pressure and temperature conditions above the Figure 1 welded with PWHT carbon steel curve. Testing of field-exposed test specimens showed HTHA of both chrome-plated and bare carbon steel samples that were totally immersed in liquid [10].

Several HTHA failures were found in liquid-filled carbon steel piping not subject to PWHT downstream of gasoline desulfurization unit reactors that were operating at hydrogen partial pressures and temperatures below the welded and PWHT carbon steel curve as it appeared in Figure 1 in previous editions of this RP. See Annex F for more discussion of non-PWHT'd carbon steel. See Annex G for more discussion on how to calculate the hydrogen partial pressure in liquid-filled equipment and piping.

3.4 Base Material for Refractory-lined Equipment or Piping

For cold-wall refractory-lined equipment or piping, there can be a risk of HTHA when:

- the internal process conditions are above the relevant carbon steel curve of Figure 1, and
- the refractory becomes degraded or there is gas bypass behind the refractory, resulting in a hot spot on the outer shell.

The materials selection for the outer shell should consider the risk and possible severity of metal hot spots due to refractory damage. The risk of hot spots is greater if the refractory is known to experience erosion or other degradation mechanisms in the specific service. The risk level may be mitigated if there are effective techniques of promptly detecting hot spots and efficient means of keeping the hot spot areas cooled. As such, owners/operators should inspect refractory-lined equipment periodically with thermography and mitigate the hot spots with air/steam to a temperature below the Nelson curve, but above any process dew point.

A more reliable way of protecting the base metal in refractory-lined equipment with a risk of HTHA is to select materials resistant to the internal hydrogen partial pressure and predicted hot spot temperatures. The design can still take advantage of higher allowable stresses at the cooler refractory-protected temperatures to enable less wall thickness, while protecting the base metal from the potential of HTHA failure.

3.5 References and Comments for Figure 1

NOTE The data points in Figure 1 are labeled with reference numbers corresponding to the sources listed in 3.5.1. The letters in the figure correspond to the comments listed in 3.5.2.

3.5.1 Figure 1 References

- 1) Shell Oil Company, private communication to API Subcommittee on Corrosion.
- 2) Timken Roller Bearing Company, private communication to API Subcommittee on Corrosion.
- 3) F.K. Naumann, "Influence of Alloy Additions to Steel Upon Resistance to Hydrogen Under High Pressure," *Technische Mitteilungen Krupp*, Vol. 1, No. 12, pp. 223–234, 1938.

- 4) N.P. Inglis and W. Andrews, "The Effect on Various Steels of Hydrogen at High Pressure and Temperature," *Journal of the Iron and Steel Institute*, Vol. 128, No. 2, pp. 383–397, 1933.
- 5) J.L. Cox, "What Steel to Use at High Pressures and Temperatures," *Chemical and Metallurgical Engineering*, Vol. 40, pp. 405–409, 1933.
- 6) R.J. Sargant and T.H. Middleham, "Steels for Autoclaves," *Chemical Engineering Congress Transactions*, Vol. I, World Power Conference, London, pp. 66–110, June 1936.
- 7) Standard Oil Company of California, private communication to API Subcommittee on Corrosion.
- 8) E.I. du Pont de Nemours and Company, private communication to API Subcommittee on Corrosion.
- 9) Ammonia-werk Merseberg, private communication to API Subcommittee on Corrosion, 1938.
- 10) Hercules Powder Company, private communication to API Subcommittee on Corrosion.
- 11) C.A. Zapffe, "Boiler Embrittlement," *Transactions of the ASME*, Vol. 66, pp. 81–126, 1944.
- 12) The M.W. Kellogg Company, private communication to API Subcommittee on Corrosion.
- 13) German operating experience, private communication to API Subcommittee on Corrosion, 1946.
- 14) Vanadium Corporation of America, private communication to API Subcommittee on Corrosion.
- 15) Imperial Chemical Industries, Billingham, England, private communication to API Subcommittee on Corrosion.
- 16) T.C. Evans, "Hydrogen Attack on Carbon Steels," *Mechanical Engineering*, Vol. 70, pp. 414–416, 1948.
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- 19) A.R. Ciuffreda and W.D. Rowland, "Hydrogen Attack of Steel in Reformer Service," *Proceedings*, Vol. 37, API, New York, pp. 116–128, 1957.
- 20) API Refinery Corrosion Committee Survey, 1957.
- 21) Air Products, Inc., private communication to API Subcommittee on Corrosion, March 1960.
- 22) G.D. Gardner and J.T. Donovan, "Corrosion and Erosion in the Synthetic Fuels Demonstration Plants," *Transactions of the ASME*, Vol. 75, pp. 525–533, 1953.
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- 24) E.W. Comings, *High Pressure Technology*, McGraw-Hill, New York, 1956.
- 25) M. Hasegawa and S. Fujinaga, "Attack of Hydrogen on Oil Refinery Steels," *Tetsu To Hagane*, Vol. 46, No. 10, pp. 1349–1352, 1960.
- 26) K.L. Moore and D.B. Bird, "How to Reduce Hydrogen Plant Corrosion," *Hydrocarbon Processing*, Vol. 44, No. 5, pp. 179–184, 1965.
- 27) Union Oil Company of California, private communication to API Subcommittee on Corrosion, 1976.
- 28) Amoco Oil Company, private communication to API Subcommittee on Corrosion, 1976.
- 29) Standard Oil Company of California, private communication to API Subcommittee on Corrosion, 1976.

- 30) Exxon Corporation, private communication to API Subcommittee on Corrosion, 1976.
- 31) Shell Oil Company, private communication to API Subcommittee on Corrosion, 1976.
- 32) Cities Service Company, private communication to API Subcommittee on Corrosion, 1976.
- 33) Gulf Oil Corporation, private communication to API Subcommittee on Corrosion, 1976.
- 34) J. McLaughlin, J. Krynicki, and T. Bruno, "Cracking of non-PWHT'd Carbon Steel Operating at Conditions Immediately Below the Nelson Curve," *Proceedings of 2010 ASME Pressure Vessels and Piping Conference, July 2010, Bellevue Washington*, PVP2010-25455.
- 35) Eight separate points 35a through 35h. Valero Energy Corporation, private communication to API Subcommittee on Corrosion, 2012.
- 36) Phillips 66 Company, private communication to API Subcommittee on Corrosion, 2012.
- 37) Phillips 66 Company, private communication to API Subcommittee on Corrosion, 2012.
- 38) Total Refining and Marketing, private communication to API Subcommittee, 2011.
- 39) Marathon Petroleum Co., private communication to API Subcommittee, 2014.
- 40) Marathon Petroleum Co., private communication to API Subcommittee, 2014.

3.5.2 Figure 1 Comments

- A) A section made of A106 pipe was found to be damaged to 27 % of its thickness after 5745 hours. Other pieces of pipe in the same line were unaffected.
- B) The damage was concentrated in the overheated section of a hot bent steel elbow. The unheated straight portions of the elbow were not attacked.
- C) In a series of 29 steel samples, 12 were damaged, while 17 were not.
- D) After 2 years exposure, five out of six pieces of carbon steel pipe were damaged. One piece of pipe was unaffected.
- E) Damage was concentrated in the weld and heat-affected sections of A106 pipe. Base metal on either side of this zone was unaffected.
- F) After 11 years of service, damage was found in the hot bent section of A106 pipe. Unheated straight sections were not affected.
- G) After 2 years of service, all parts of carbon steel pipe, including weld and heat-affected zone (HAZs), were satisfactory.
- H) After 4 years of service, weld and HAZs of A106 pipe showed cracks.
- J) After 31 years of service, a forging of 0.3C-1.3Cr-0.25Mo steel showed cracks 0.007 in. (0.2 mm) deep.
- K) Pipes of 1.25Cr-0.25Mo steel.
- L) After 4 years of service, a forging of 0.3C-1.3Cr-0.25Mo steel was unaffected.
- N) After 7 years of service, a forging of 0.3C-1.52Cr-0.50Mo steel showed cracks 0.050 in. (1.3 mm) deep.

- P) After 30 years of service, a forging of 0.30C-0.74Cr-0.43Ni steel was unaffected.
- Q) After 15 years in ammonia service, a pipe of 0.15C-2.25Cr-1.00Mo steel showed no HTHA but was nitrided to a depth of 0.012 in. (0.3 mm).
- S) After 8 years, carbon steel cracked.
- T) After 18 years, carbon steel did not show HTHA.
- U) After 450 days exposure, a 1.25Cr-0.5Mo valve body was not damaged by HTHA.
- V) Point 34. After 30+ years non-PWHT'd carbon steel reactor, vessels, and associated piping in light distillate hydrotreating service cracked from HTHA. Operating at roughly 580 °F (304 °C) and at 125 psia (0.86 MPa).
- W) Points 35a and 35h. These 2 points on the plot represent the range of 8 different failures. After 4.5 to 8 years, 7 different non-PWHT'd carbon steel flanges cracked in the HAZs on the flange side of a flange-to-pipe weld in gasoline hydrotreating service. One cracked on the pipe side of the pipe-to-flange weld. Operating at roughly 645 °F (340 °C) and at 57 psia to 94 psia (0.39 MPa to 0.65 MPa) hydrogen partial pressure.
- X) Point 37. After 14 years, a non-PWHT'd SA-105 carbon steel flange cracked in the HAZ on the flange side of a flange-to-pipe weld. Operating at roughly 600 °F (316 °C) and at 280 psia (1.9 MPa).
- Y) Point 36. After 6 years, multiple non-PWHT'd carbon steel flanges cracked in the HAZs on the flange side of a flange to pipe welds in a gasoline desulfurization unit. Operating at roughly 670 °F (354 °C) and at 85 psia (0.59 MPa).
- Z) Point 38. After 29 years, a non-PWHT'd carbon steel exchanger shell in Hydrodesulfurization (HDS) service cracked. Operating at roughly 500 °F (260 °C) and at 670 psia (4.6 MPa).
- A.1) Point 39. After 10 years, inspection found cracks in a non-PWHT'd carbon steel exchanger shell in light hydrotreater service. Operating at roughly 540°F (282 °C) and at 130 psia (0.90 MPa).
- B.1) Point 40. After 30+ years, inspection found cracks in a non-PWHT'd carbon steel exchanger shell in light hydrotreater service. Operating at roughly 490 °F (254 °C) and at 195 psia (1.3 MPa).

4 Forms of HTHA

4.1 General

High temperature hydrogen can attack steels in two ways:

- a) surface decarburization, and
- b) internal decarburization and fissuring, eventually leading to cracking.

The combination of high temperature and low hydrogen partial pressure favors surface decarburization without internal decarburization and fissuring. The combination of low temperature, but above 400 °F (204 °C), and high hydrogen partial pressure, above 2200 psia (15.17 MPa), favors internal decarburization and fissuring, which can eventually lead to cracking. At high temperatures and high hydrogen partial pressures, both mechanisms are active. These mechanisms are described in detail below.

The broken-line curves at the top of Figure 1 represent the tendencies for surface decarburization of steels while they are in contact with hydrogen. The solid-line curves represent the tendencies for steels to decarburize internally with resultant fissuring and cracking.

4.2 Surface Decarburization

Surface decarburization without fissuring has been associated with hydrogen partial pressure and temperature conditions that are not severe enough to generate the methane pressures needed to form fissures. This typically occurs in carbon steel where the Nelson curves become vertical [39].

Surface decarburization as a form of HTHA is similar to that resulting from the high-temperature exposure of steel to certain other gases such as air, oxygen, or carbon dioxide. The usual effects of surface decarburization are a slight, localized reduction in strength and hardness and an increase in ductility. Because these effects are usually small, there is often much less concern with surface decarburization than there is with internal decarburization.

A number of theories have been proposed to explain surface decarburization [2] [3] [4], but the currently accepted view is based on the migration of carbon to the surface where gaseous compounds of carbon are formed, rendering the steel less rich in carbon. The gaseous compounds formed are CH_4 or, when oxygen-containing gases are present, CO . Water vapor hastens the reaction. While carbon in solution diffuses to the surface to form gaseous carbon compounds, the carbon in solution is continuously supplied from the carbide compounds in the steel. Thus, carbide stability is directly related to the rate of surface decarburization.

In cases where surface decarburization predominates over internal attack, the actual values of pressure-temperature combinations have not been extensively studied, but the limits defined by Naumann [5] probably give the most accurate trends.

4.3 Internal Decarburization, Fissuring, and Cracking

The solid-line curves in Figure 1 define the areas above which material damage by internal decarburization and fissuring/cracking have been reported. Below and to the left of the curve for each alloy, satisfactory performance has been experienced with periods of exposure of up to approximately 60 years. At temperatures above and to the right of the solid curves, there is a probability that internal decarburization and fissuring/cracking may occur. Internal decarburization and fissuring are preceded by a period of time where no immediate damage is detected, and this is often referred to as an “incubation period.” The incubation period depends on temperature and hydrogen partial pressure (see 5.1 for further discussion).

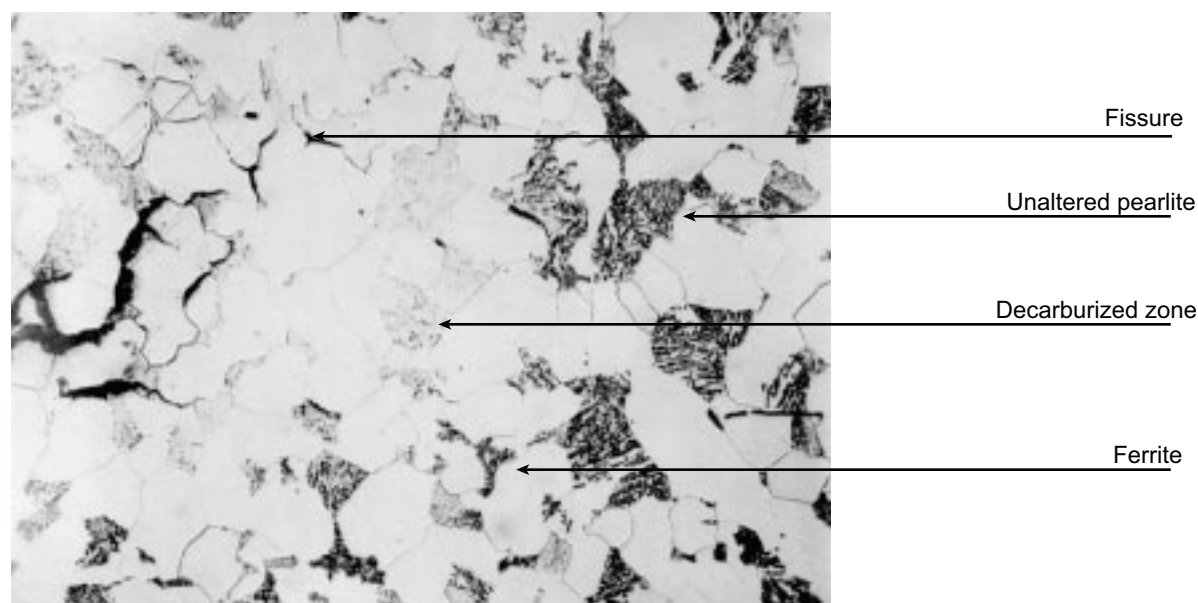
Internal decarburization and fissuring are caused by hydrogen permeating the steel and reacting with carbon to form methane [5]. The methane formed cannot diffuse out of the steel and typically accumulates at grain boundaries. This results in high localized stresses that lead to the formation of fissures, cracks, or blisters in the steel. Fissures in hydrogen-damaged steel lead to a substantial deterioration of mechanical properties.

Figure 2 shows the microstructure of a sample of C-0.5Mo steel damaged by internal decarburization and fissuring. The service conditions were 790 °F (421 °C) at a hydrogen partial pressure of 425 psia (2.9 MPa) for approximately 65,000 hours in a catalytic reformer.

The addition of carbide stabilizers to steel reduces the tendency toward internal fissuring. Elements, such as chromium, molybdenum, tungsten, vanadium, titanium, and niobium, form more stable alloy carbides that resist breakdown by hydrogen and thereby decrease the propensity to form methane [6]. The solid-line curves in Figure 1 reflect the increased resistance to internal attack when molybdenum and chromium are present.

The presence of nonmetallic inclusions tends to increase the extent of blistering damage. If steel contains segregated impurities, stringer-type inclusions or laminations then severe blistering may in these areas from hydrogen or methane accumulation [7].

Alloys other than those shown in Figure 1 may also be suitable for resisting HTHA. These include modified carbon steels and low alloy steels to which carbide stabilizing elements (molybdenum, chromium, vanadium, titanium, or niobium) have been added such as some European alloys [8]. Austenitic stainless steels are resistant to decarburization, even at temperatures above 1000 °F (538 °C) [9].



NOTE Service conditions were 65,000 hours in a catalytic reformer at a temperature of 790 °F (421 °C) and a hydrogen partial pressure of 425 psia (2.9 MPa). From Reference [11] in the Bibliography. Magnification: 520X; nital etched.

Figure 2—C-0.5Mo Steel (ASTM A204 Grade A) Showing Internal Decarburization and Fissuring in High Temperature Hydrogen Service

5 Factors Influencing Internal Decarburization, Fissuring, and Cracking Caused by HTHA

5.1 Incubation Time

Internal HTHA begins once the service conditions (high pressure and high temperature hydrogen) are such that the hydrogen diffused into the steel begins to react with the carbon or carbides in the steel. In the initial stages of attack, there is a period of time where the damage is so microscopic that it cannot be detected by current nondestructive examination (NDE) and metallographic technology. Beyond this there is also a period when no noticeable change in mechanical properties is detectable by current testing methods. After this period of time has elapsed, material damage is evident with resultant decreases in strength, ductility, and toughness. This varies with the type of steel and severity of exposure; it may take only a few hours under extreme conditions and take progressively longer at lower temperatures and hydrogen partial pressures. With some steels under mild conditions, no damage can be detected even after many years of exposure. During this initial stage of attack, in some cases, laboratory examination (high magnification metallography, utilizing optical microscopy and scanning electron microscopy) of samples removed from the equipment have revealed the initial stages of attack with voids at grain boundaries.

The period of time until mechanical damage can be detected is commonly referred to as the “incubation time” in the petrochemical industry. The length of the incubation period is important because it determines the useful life of a steel at conditions under which internal HTHA occurs. Useful theoretical models of the HTHA mechanism and incubation period have been proposed [11] [12] [13] [39].

Internal HTHA can be viewed as occurring in four stages:

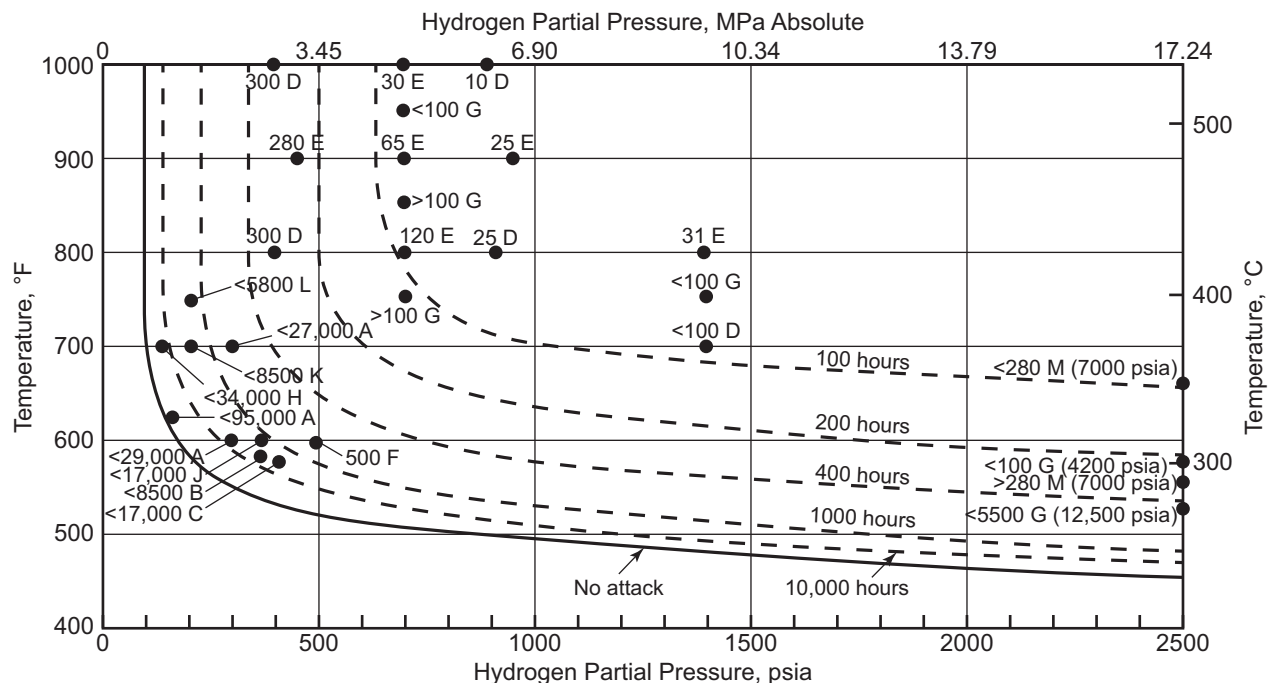
- the incubation period during which the microscopic damage cannot be detected with advanced NDE techniques and the mechanical properties are not affected;
- the stage where damage is detectable optically (<1000X), possibly detectable by advanced NDE techniques, and mechanical properties are partially deteriorated;

- c) the stage of rapid mechanical property deterioration associated with rapid fissure growth; and
- d) the final stage where carbon in solid solution is reduced to compromise material mechanical properties to a level where cracking can occur.

During the incubation period, methane pressure builds up in submicroscopic voids. These voids grow slowly due to both internal methane pressure and applied stress. When the voids reach a critical size and begin connecting to form fissures, the effects on mechanical properties become evident. The incubation period depends on many variables including the type of steel, degree of cold working, amount of impurity elements, applied stress, hydrogen pressure, and temperature.

Incubation curves for non-welded or welded with PWHT carbon steel are given in Figure 3. These can be used as a guide in determining approximate safe operating times when PWHT'd carbon steel equipment operates above its curve in Figure 1. Annex A includes similar curves that may be useful for some heats of C-0.5Mo steel, with the precaution that the resistance of C-0.5Mo steel to HTHA is particularly sensitive to heat treatment, chemical composition, and the heating/cooling history of the steel during forming [15] [16] [17] [18]. API Technical Report (TR) 941, *The Technical Basis Document for API RP 941*, provides additional guidance on safe operating times for steels above their respective curves in Figure 1.

The Figure 3 [14] and Annex A incubation curves, as well as the guidance in API TR 941, are commonly used to evaluate unintentional upsets and short-term intentional operating periods such as during start-up of a process unit and elevated temperatures at end of run. Recent experience with HTHA in liquid-filled hydrocarbon service showed that HTHA occurred much more rapidly than what these curves predict. Incubation curves should not be used for liquid-filled streams.



NOTE 1 the letter "I" is not used

NOTE 2 This figure first appeared as Figure 4 in the first edition (1970) of this publication.

NOTE 3 See Section 6.2 for references related to this figure.

Figure 3—Incubation Time for High Temperature Hydrogen Attack Damage of Carbon Steel (Non-welded or Welded with Postweld Heat Treatment) in High Temperature Hydrogen Service

5.2 Effect of Primary Stresses

Primary stresses are design stresses imposed by internal pressure, nozzle loadings, and the like. While it is known that very high stress levels can accelerate the rate of HTHA development (see, for example, Annex C), long-term operating experience dating from before 1969 has demonstrated that equipment designed within the allowable stresses of the relevant ASME Codes, which include ASME Section VIII Divisions 1 and 2 for pressure vessels and ASME B31.3 for piping, as well as equivalent foreign national codes, will perform satisfactorily when operated within the temperature and hydrogen partial pressure limits given in Figure 1 for the particular steel.

ASME Section VIII Division 2 has higher allowable design stresses than Division 1 and is typically used for high pressure, high temperature, thick-wall pressure vessels made of Cr-Mo steels. The Cr-Mo steels typically receive a normalized and tempered (N&T) or quenched and tempered (Q&T) heat treatment to provide improved fracture toughness, as well as slightly higher strength, as compared to carbon steel. Cr-Mo steel vessels designed to the higher allowable stress levels of Division 2 have a long, successful history of resistance to HTHA, as long as stresses are within the ASME Code allowable limits (or similar allowable limits in equivalent non-ASME Codes) and when operated within the temperature and hydrogen partial pressure limits given in Figure 1. This is evidenced by the lack of internal decarburization and fissuring data points for the steels in Figure 1.

While unusually high localized stresses have, in rare cases, caused HTHA in 2.25Cr-1Mo steel under temperature and hydrogen partial pressure conditions not expected to cause damage according to Figure 1 [23], there is no report of HTHA below the Figure 1 limits when stresses are within the design limits of the ASME Code.

Research studies [19] [20] [21] [22] have shown that creep strength and ductility of 2.25Cr-1Mo steel are diminished in very high pressure H₂ as compared to air. However, as long as operating temperatures are kept below the 850 °F (454 °C) limit given in Figure 1, creep of 2.25Cr should not be an issue.

5.3 Effect of Secondary Stresses

HTHA can be accelerated by secondary stresses such as thermal stresses or those induced by cold work. High thermal stresses were considered to play a significant role in the HTHA of some 2.25Cr-1Mo steel piping [24]. Other 2.25Cr-1Mo steel piping in the same system, subjected to more severe hydrogen partial pressures and temperatures, was not attacked.

The effect of cold work was demonstrated by Vitovec in research sponsored by API and summarized in API 940 [6]. Vitovec compared specific gravities of SAE 1020 steel with varying degrees of cold work tested in 900 psi (6.2 MPa) hydrogen at 700 °F (371 °C), 800 °F (427 °C), and 1000 °F (538 °C). The decrease in specific gravity over time indicates the rate at which internal fissures are produced by HTHA. Annealed samples (0 % strain) had an incubation period followed by a decrease in specific gravity. Steels with 5 % strain had shorter incubation periods and specific gravity decreased at a more rapid rate. Steels with 39 % strain showed no incubation period at any test temperature, indicating that fissuring and cracking started immediately upon exposure to hydrogen.

These tests are considered significant in explaining the cracks sometimes found in highly stressed areas of an otherwise apparently resistant material. In addition, Cherrington and Ciuffreda [25] have emphasized the need for removing notches (stress concentrators) in hydrogen service equipment.

5.4 Effect of Heat Treatment

Both industry experience and research indicate that PWHT of steels (carbon steels, C-0.5Mo steels and chromium-molybdenum steels) in hydrogen service improves resistance to HTHA. The PWHT stabilizes alloy carbides. This reduces the amount of carbon available to combine with hydrogen, thus improving HTHA resistance. Also, PWHT reduces residual stresses and is, therefore, beneficial for all steels.

Research [4] [13] [17] [18] [26] has shown that certain metal carbides may be more resistant to decomposition in high temperature hydrogen environments. Creep tests in hydrogen demonstrated the beneficial effect of increased PWHT on the HTHA resistance of 2.25Cr-1Mo steel [19]. In these tests, 2.25Cr-1Mo steels PWHT'd for 16 hours at 1275 °F

(691 °C) showed more resistance to HTHA than the same steels PWHT'd for 24 hours at 1165 °F (630 °C). While PWHT for longer duration showed some beneficial effect, high PWHT temperatures have a more beneficial effect on HTHA resistance. Similarly, HTHA resistance of 1Cr-0.5Mo and 1.25Cr-0.5Mo steels is improved by raising the minimum PWHT temperature to 1250 °F (677 °C) from the 1100 °F (593 °C) minimum required by past additions of Section VIII of the ASME Code.

The user must balance the advantages of high PWHT temperatures with other factors such as the effect upon strength and notch toughness.

NOTE Note higher PWHT temperatures can affect the ability to meet ASME Code Class 2 strength requirements, and the strength requirements of enhanced grades of low alloy steels.

Local PWHT bands often do not effectively reach desired temperatures throughout the weldment. In order to improve the effectiveness of PWHT, the band widths shall be increased as recommended by American Welding Society (AWS) D10.10 for piping and Welding Research Council (WRC) 452 for vessels. For each PWHT, three different band widths are specified in these standards, namely soak band, heating band, and gradient control band. The recommended thermocouple placements in these standards shall also be followed.

5.5 Effect of Stainless Steel Cladding or Weld Overlay

The solubility of hydrogen in austenitic stainless steel is about an order of magnitude greater than for ferritic steels [27]. The diffusion coefficient of hydrogen through austenitic stainless steel is roughly two orders of magnitude lower than for ferritic steels [28] [29] [39]. This can result in a significant reduction in the effective hydrogen partial pressure experienced by the underlying steel below the cladding.

Ferritic or martensitic stainless steel (400 Series) claddings or weld overlays have similar solubilities and diffusivities than the underlying ferritic steel [39] [41]. As a result, the only reduction in hydrogen partial pressure realized for ferritic or martensitic cladding is roughly equal to the ratio of the cladding to the base metal as follows:

$$P_{\text{eff}} = P_{\text{H}_2} \left(\frac{t_{\text{base metal}}}{t_{\text{base metal}} + t_{\text{cladding}}} \right)$$

where

P_{H_2} is the hydrogen partial pressure,

P_{eff} is the effective hydrogen partial pressure,

$t_{\text{base metal}}$ is the thickness of base metal,

t_{cladding} is the thickness of clad/overlay.

A sound metallurgically bonded austenitic stainless steel cladding or weld overlay can significantly reduce the effective hydrogen partial pressure acting on the base metal. The amount of hydrogen partial pressure reduction depends upon the materials and the relative thickness of the cladding/weld overlay and the base metal. The thicker the stainless steel barrier is relative to the base metal, the lower the hydrogen concentration [30] [39]. Archakov and Grebeshkova [31] mathematically considered how stainless steel corrosion barrier layers increase resistance of carbon and low alloy steels to HTHA. The calculation for determining the effective hydrogen pressure at the clad/weld overlay-to-base metal interface is presented in Annex D.

There have been a few instances of HTHA of base metal that was clad or overlaid with austenitic stainless steel. All of the reported instances involved C-0.5Mo steel base metal. In one case [32], HTHA occurred in a reactor vessel at a nozzle location where the C-0.5Mo base metal was very thick, relative to the cladding/overlay. Another incident of HTHA of C-0.5Mo steel occurred under intergranularly cracked Type 304 austenitic stainless steel cladding (see data point 51U in Annex A). The other cases involved ferritic or martensitic stainless steel cladding.