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 referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) 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*

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[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:

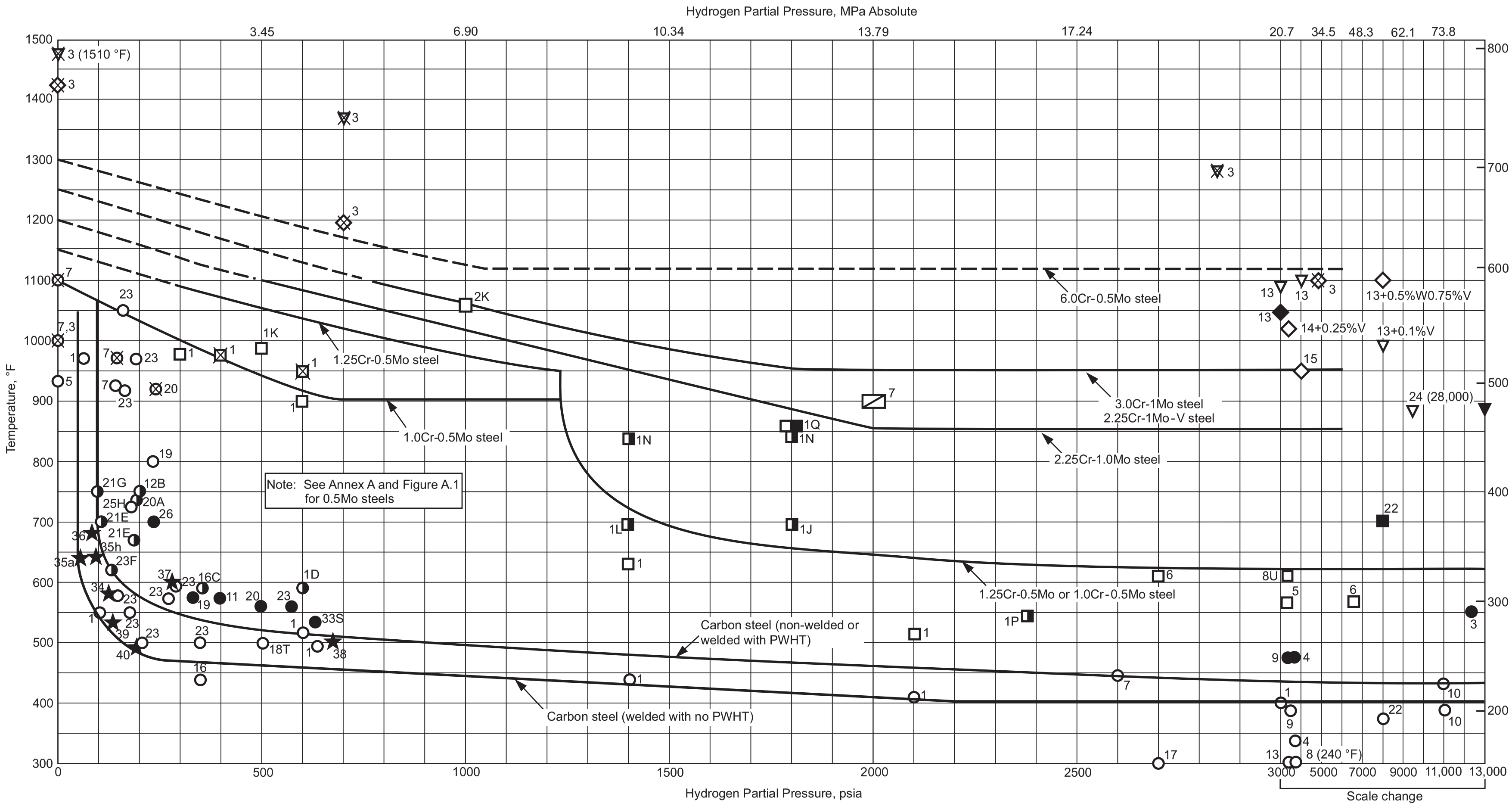
a) other corrosive species that may be in the system such as hydrogen sulfide;

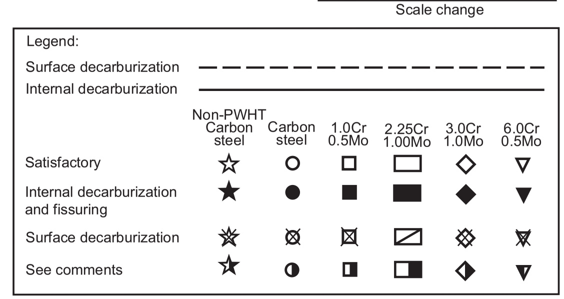
b) creep, temper embrittlement, or other high temperature damage mechanisms;

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.





NOTE 1 The limits described by these curves are based on service experience originally collected by G.A. Nelson and on additional information gathered by or made available to API.

NOTE 2 Austenitic stainless steels are generally not decarburized in hydrogen at any temperature or hydrogen pressure.

NOTE 3 The limits described by these curves are based on experience with cast steel as well as annealed and normalized steels at stress levels defined by Section VIII, Division 1, of the ASME Code. See 5.3 and 5.4 in text for additional information.

NOTE 4 Several failures of 1.25Cr 1-Mo steel have been reported in the satisfactory region. See Annex B for details.

NOTE 5 The inclusion of the 2.25Cr-1Mo-V class of steels is based on 10,000+hr laboratory tests where these alloys were at least equal to the 3Cr-1Mo steel. See Reference [22] listed in the Bibliography.

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 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 Mitieilungen 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) Ammoniawerk 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.

17) Norweg Hydroelectric, Oslo, Norway, private communication to API Subcommittee on Corrosion.

18) Union Oil Company of California, private communication to API Subcommittee on Corrosion, 1980.

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.

23) Amoco Oil Company, private communication to API Subcommittee on Corrosion, 1960.

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 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).

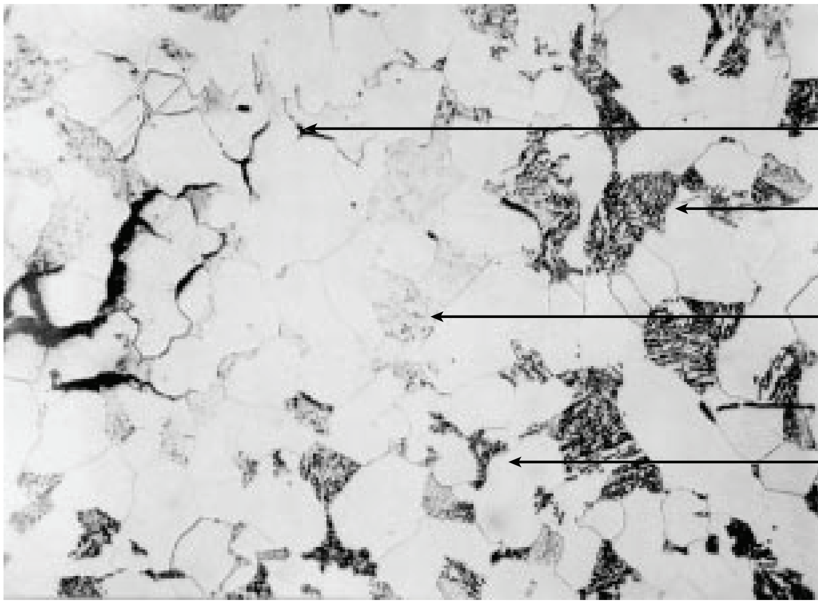
Internal decarburization and fissuring are caused by hydrogen permeating the steel and reacting with carbon to form methane [5]. The methane formed cannot diffuse out of the steel and typically accumulates at grain boundaries. This results in high localized stresses that lead to the formation of fissures, 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 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:

a) the incubation period during which the microscopic damage cannot be detected with advanced NDE techniques and the mechanical properties are not affected;

b) 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 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.

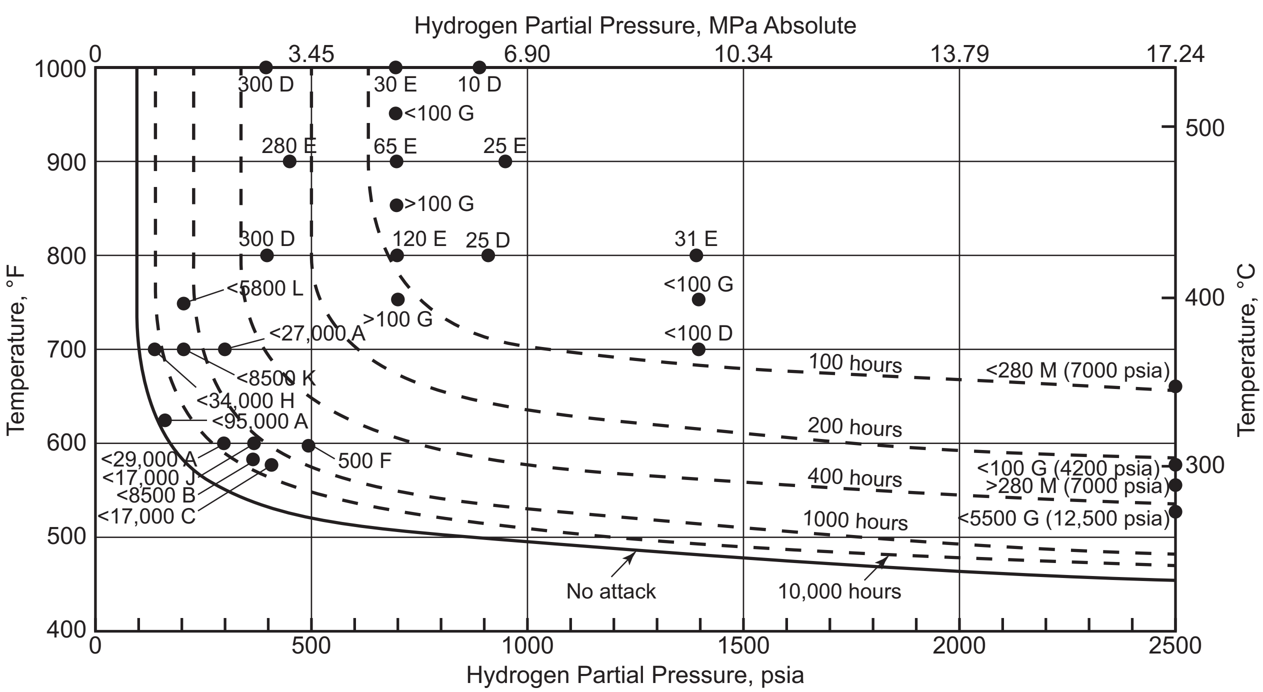


Figure 3—Incubation Time for High Temperature Hydrogen Attack Damage of Carbon Steel (Non-welded or Welded with Postweld Heat Treatment) in High Temperature Hydrogen Service

(see 6.2 for references for this figure)

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 H_2 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:

$$P_{\text{eff}} = P_{\text{H2}}\left(\frac{t_{\text{base metal}}}{t_{\text{base metal}} + t_{\text{cladding}}}\right)$$

where

P_{H2} 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 overlayed 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.

It is not advisable to take a credit for the presence of a stainless steel cladding/weld overlay when selecting the base metal for a new vessel. Some operators have successfully taken credit for the presence of an austenitic stainless steel cladding/weld overlay for operation when conditions exceeded the Figure 1 curve for the base metal. Satisfactory performance in such cases requires assurance that the effective hydrogen partial pressure acting on the base metal be accurately determined and that the integrity of the cladding/weld overlay be maintained. Such assurance may be difficult to achieve, especially where complex geometries are involved. Many operators take the presence of an austenitic stainless steel cladding/weld overlay into account when establishing inspection priorities for HTHA, especially for C-0.5Mo steel equipment.

More background information and details about many of these factors can be found in API TR 941 [39].

6 Inspection for HTHA

6.1 General

The selection of optimum inspection methods and frequencies for HTHA in specific equipment or applications is the responsibility of the user. The information below and in Annex E, Table E.1 and Table E.2 are intended to assist the user in making such decisions. The user is also referred to API TR 941, Annex C, “Estimating Damage Rates for Life Assessment” [39]. This damage rate model may assist in determining inspection needs and prioritization.

Most users do not inspect equipment for HTHA damage unless it has been operated near or above its curve. An HTHA inspection program should also consider equipment that operates infrequently above its curve (e.g. operations such as “hot hydrogen stripping” in hydroprocessing reactors and associated piping and equipment). Only a small number of documented instances of HTHA occurring at conditions below the curves have been reported to API (see Annex A, Annex B, Annex C, and Annex F). Most of these have involved C-0.5Mo steel [33] or non-PWHT’d carbon steel [40]. Periodic inspection of C-0.5Mo steel equipment and piping should be considered if operated above the carbon steel curve, based on factors such as relative position of the operating parameters versus the carbon steel curve, consequence of failure, presence of cladding, prior heat treatment, etc. Because it is time dependent, existing C-0.5Mo steel equipment and piping may continue to deteriorate with time, if susceptible. As this equipment and piping age, the owner should consider increasing the inspection frequency (also see Annex A).

HTHA damage may occur in welds, weld HAZs, or base metal. Even within these specific areas, the degree of damage may vary widely. Consequently, if damage is suspected, then a thorough inspection means that representative samples of these areas be examined.

Table E.1 and Table E.2 provide a summary of available methods of inspection for HTHA damage and includes a discussion of the advantages and limitations of each. While ultrasonic testing (UT) methods, as described in Table E.1, are the most effective for detecting internal HTHA damage, two or more inspection methods are often used in combination to overcome the limitations of any single method [34] [35].

HTHA is a difficult inspection challenge. The early stages of attack with fissures, or even small cracks, can be difficult to detect. The advanced stage of attack, with significant cracking, is much easier to detect, but at that point there is already a higher likelihood of equipment failure. In addition to attack of the base metal, HTHA has been known to occur as a very narrow band of intense attack and cracking, running alongside and parallel to welds.

Of all the inspection methods for base metal examination, UT methods have the best chance of detecting HTHA damage while it’s still in the fissuring stage, prior the onset of significant cracking. Most effective is the use of a frequency dependent backscatter method in combination with the velocity ratio and spectral analysis techniques. Backscatter can be used as a first step of inspection and can be used to quantify the depth of damage. Velocity ratio and spectral analysis are useful for confirmation of backscatter indications. Other methods are capable of detecting HTHA only after discrete cracks have formed and there is significant degradation of mechanical properties.

For weldment examination where attack can be highly localized, as mentioned above, only two UT methods of examination are considered effective. High frequency shear wave and angle-beam spectrum analysis techniques should be used to detect HTHA damage in the fissuring stage [36] [37]. Conventional shear wave UT and time of flight diffraction (TOFD) techniques can be used to try to detect HTHA in the advanced stages, when there is significant cracking.

When the internal surface is accessible, wet fluorescent magnetic particle testing (WFMT) can be used to find HTHA damage in the form of surface breaking cracks. Close visual inspection can detect small coin-sized surface blisters, which can be an indication of the presence of internal HTHA. In situ metallography can be effective in detecting the early stages of HTHA (decarburization and fissuring) at the surface of the steel as well as differentiating between HTHA and other forms of cracking. Skill is required for the surface polishing, etching, replication, and microstructural interpretation. Because in situ metallography only examines a small specific area, other methods should be used to complement it. It requires access to the surface of interest, and may require removal of a small amount of surface material from the process side for best results (see Table E.2). One note of caution is that HTHA may be subsurface; using a surface inspection technique, such as replication or WFMT, may not detect damage. Another is that the absence of surface blisters does not ensure that internal HTHA is not occurring, since HTHA frequently occurs without the formation of surface blisters.

6.2 References

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Annex A
(informative)

HTHA of 0.5Mo Steels

A.1 General

The purpose of this annex is to provide a brief summary of the information and experience regarding the use of 0.5Mo (C-0.5Mo and Mn-0.5Mo) steels in elevated temperature and pressure hydrogen service.

Most companies no longer specify C-0.5Mo steel for new or replacement equipment used for operation above the PWHT'd carbon steel curve in Figure 1 because of the uncertainties regarding its performance after prolonged use. Since 1970, a series of unfavorable service experiences with C-0.5Mo steels has reduced confidence in the position of the 0.5Mo curve [40] [41]. In the Second Edition (1977) of this publication, the 0.5Mo curve was lowered approximately 60 °F (33 °C) to reflect a number of plant experiences that involved HTHA of C-0.5Mo equipment. In the Fourth Edition (1990) of this publication, the 0.5Mo curve was removed from Figure 1 due to additional cases of HTHA of C-0.5Mo steel equipment occurring by as much as 200 °F (111 °C) below the curve. At that time, experience had identified 27 instances of HTHA below the 1977 curve. The operating conditions for these instances are given in Table A.1 and are plotted on Figure A.1.

No instances of HTHA have been reported using Mn-0.5Mo steel operating below the Figure A.1 0.5Mo curve. The information and use of this material at elevated temperatures and hydrogen partial pressures are limited.

C-0.5Mo steels vary in their resistance to HTHA. Many heats seem to have resistance at conditions indicated by the 0.5Mo curve in Figure A.1. However, some heats seem to have HTHA resistance only marginally better than carbon steel. Published works [41] [42] [43] [44] suggest a correlation between thermal history of the steel and its resistance to HTHA. Slow-cooled, annealed C-0.5Mo steels have less resistance to HTHA than normalized steels. The studies have shown that PWHT improves the HTHA resistance of weldments and HAZs for both annealed and normalized C-0.5Mo steels. However, the base metals of slow-cooled, annealed C-0.5Mo steels show a decrease in HTHA resistance after PWHT. The initial studies suggest that this is due to free carbon being present in the ferrite matrix after PWHT. Normalized C-0.5Mo steel base metals, on the other hand, show improvement in HTHA resistance following tempering or PWHT. Such normalized and PWHT'd C-0.5Mo steel appears to have hydrogen attack resistance about as indicated by the 0.5Mo curve in the Second Edition (1977) of this publication. Until the factors controlling the HTHA resistance of C-0.5Mo are better understood, each user should carefully assess the use of C-0.5Mo steel in services above the PWHT'd carbon steel curve in Figure 1.

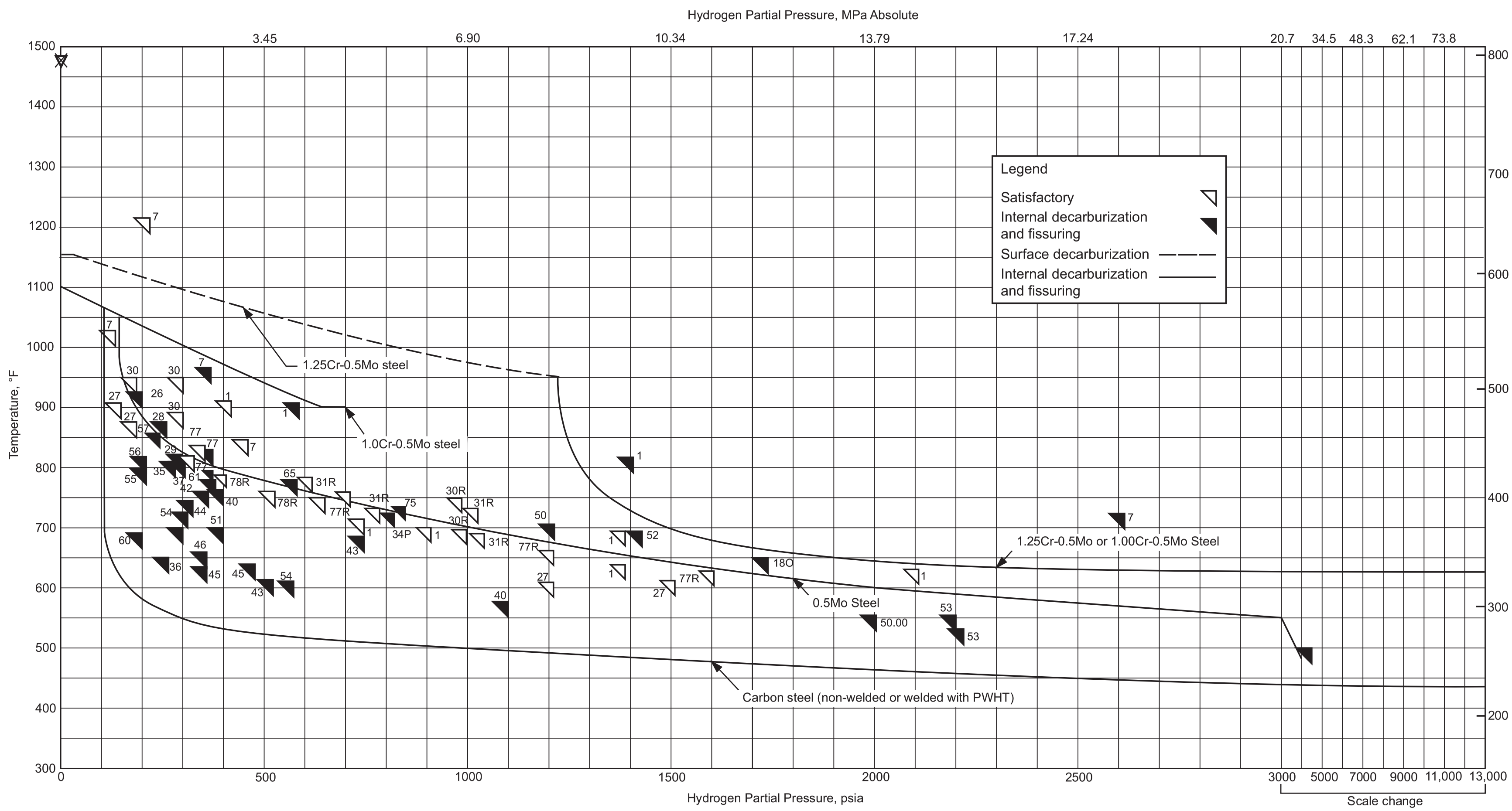
Existing C-0.5Mo steel equipment that is operated above the PWHT'd carbon steel curve in Figure 1 should be inspected to detect HTHA. Owners/operators should evaluate and prioritize for inspection C-0.5Mo equipment operating above the carbon steel limit—Hattori and Aikawa [45] addressed this issue. The work cited above and plant experience suggest that important variables to consider in prioritizing equipment for inspection include severity of operating condition (hydrogen partial pressure and temperature), thermal history of the steel during fabrication, stress, cold work, and cladding composition and thickness, when present.

To provide a historical summary of the data regarding the use of C-0.5Mo steels, two additional figures are included here:

a) Figure A.2, which shows the effect of trace alloying elements and molybdenum on PWHT'd carbon steel operating limits; and

b) Figure A.3, which shows HTHA incubation times for C-0.5Mo steels.

Figure A.2 is from the second edition of this publication (1977) and is a revision of a similar figure from the original edition (1970). Figure A.2 shows that molybdenum has long been considered to be beneficial to the HTHA resistance



NOTE 1 References and comments are shown on Table A.1.

NOTE 2 Curves for carbon steel, 1.0Cr-0.5Mo steel, and 1.25 Cr-0.5Mo steel are included for reference.

NOTE 3 The symbol ◸ is retained as a reference against previous editions of this publication.

NOTE 4 Reference numbers are the same as in previous editions of this publication.

NOTE 5 The 0.5Mo steel curve is the same as the one shown in the Seventh Edition of this publication (2008).

This figure was revised by API in 1969, 1983, 1990, 1996, and 2015.

Figure A.1—Experience with C-0.5Mo and Mn-0.5Mo Steel in High Temperature Hydrogen Service

of steels. The data in Figure A.3 should be used with caution, since some heats of C-0.5Mo steels have suffered HTHA during exposure to conditions under the lower solid curve (equivalent to the C-0.5Mo curve of Figure A.1). The data for the instances of HTHA listed in Table A.1 and plotted on Figure A.1 are also shown for reference in Figure A.3. In these cases, the service life at the time the attack was detected was less than the incubation time indicated by the curves, which, of course, is not possible.

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A.3 References and Comments for Figure A.1

NOTE The data in Figure A.1 are labeled with the reference numbers corresponding to the sources listed below. The letters in the figure correspond to the comments listed on this page.

A.3.1 References

1) Shell Oil Company, private communication to API Subcommittee on Corrosion.

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18) Union Oil Company of California, private communication to API Subcommittee on Corrosion, 1980.

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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.

34) Koch Refining Company, private communication to API Subcommittee on Corrosion, 1980.

36) [A]Texaco Incorporated, private communication to API Subcommittee on Corrosion, 1980.

37) [B]Exxon Corporation, private communication to API Subcommittee on Corrosion, 1979.

38) [C]Exxon Corporation.

39) [D]Exxon Corporation.

41) [F]Caltex Petroleum Corporation, private communication to API Subcommittee on Corrosion, 1980.

42) [G]Getty Oil Company.

43) [H]Getty Oil Company.

44) [I]Caltex Petroleum Corporation, private communication to API Subcommittee on Corrosion and Materials Engineering, 1984.

45) [J]JGC Corporation/Japan Steel Works, API Midyear Refining Meeting, 1984.

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56) [CC]Chevron Research and Technology Company, private communication to API Subcommittee on Corrosion and Materials, June 1992.

57) [DD]Chevron Research and Technology Company, private communication to API Subcommittee on Corrosion and Materials, June 1992.

58) [EE]Chevron Research and Technology Company, private communication to API Subcommittee on Corrosion and Materials, June 1992.

59) [FF]Chevron Research and Technology Company, private communication to API Subcommittee on Corrosion and Materials, June 1992.

60) [GG]Chevron Research and Technology Company, private communication to API Subcommittee on Corrosion and Materials, June 1992.

61) [HH]Chevron Research and Technology Company, private communication to API Subcommittee on Corrosion and Materials, June 1992.

62) [II]Chevron Research and Technology Company, private communication to API Subcommittee on Corrosion and Materials, June 1992.

63) [JJ]Tosco, private communication to API Subcommittee on Corrosion and Materials, April 1993.

64) [KK]Tosco, private communication to API Subcommittee on Corrosion and Materials, April 1993.

65) [LL]Exxon report: "Hydrogen Attack of Gofiner Reactor Inlet Nozzle," 1988.

A.3.2 Comments

A) Feed line pipe leaked; isolated areas damaged. Blistered, decarburized, fissured; PWHT'd at 1100 °F to 1350 °F.

B) Effluent line, pipe and HAZ, isolated areas damaged; no PWHT.

C) Weld and pipe, isolated areas damaged; no PWHT.

D) Effluent line; weld, isolated areas damaged; PWHT.

E) Feed line; weld and HAZ, isolated areas damaged; PWHT.

F) Feed/effluent exchanger nozzle-to-shell weld, cracks in welds and in exchanger tubes.

G) Effluent exchanger channel; welds, plate, and HAZ, isolated areas damaged; PWHT.

H) Effluent exchanger channel; welds, plate, and HAZ, isolated areas damaged; PWHT'd at 1100 °F.

I) Catalytic reformer, combined feed/effluent exchanger shell; plate; PWHT'd at 1250 °F.

J) Hydrodesulfurization unit effluent exchanger channel head and shell plate. (Hydrocarbon feed to unit and makeup hydrogen from ethylene unit.)

K) Catalytic reformer combined feed piping; welds and base metal; PWHT.

L) Gas-oil hydrodesulfurization unit. Elbow cracked intergranularly and decarburized at fusion line between weld metal and HAZ; no PWHT.

M) Ammonia plant converter; exit piping; intergranular cracking and internal decarburization of pipe.

P) Hydrodesulfurization unit hydrogen preheat exchanger shell; blisters, intergranular fissuring, and decarburization in weld metal; PWHT'd at 1150 °F.

Q) Attack of heat exchanger tubing in tubesheet.

R) Stainless steel cladding on 0.5Mo steel; no known HTHA.

S) Decarburization and fissuring of weld metal; PWHT'd at 1150 °F.

T) Forged tubesheet cracked with surface decarburization; tubes blistered.

U) Hydrodesulfurization unit, C-0.5Mo steel exchanger tubesheet; decarburized, fissured, and cracked under intergranularly cracked ASTM Type 304 cladding.

V) Hydrocracker charge exchanger liquid with a small amount of hydrogen; C-0.5Mo with Type 410S rolled bond clad. Extensive blistering and fissuring under clad.

W) C-0.5Mo steel piping in ammonia plant syngas loop; decarburized and fissured.

AA) Blistering and fissuring of a flange.

BB) HAZ and base metal fissuring of pipe.

CC) Base metal fissuring and surface blistering in heat exchanger shell.

DD) Attack at weld, HAZ and base material in piping.

EE) Localized attack in weld, HAZ in piping.

FF) Base metal attack in piping.

GG) Base metal attack in a heat exchanger channel.

HH) Base metal attack in piping.

II) Blistering and base metal attack in a heat exchanger shell.

JJ) Base metal attack in a TP405 roll bond clad vessel.

KK) Base metal attack in a TP405 roll bond clad vessel.

LL) Attack in nozzle attachment area of a vessel weld overlaid with Type 309Nb.

MM) Internal decarburization/fissuring of piping in a hydrocracker unit after 235,000 hours of service.

Table A.1—Operating Conditions for C-0.5Mo Steels That Experienced High Temperature Hydrogen Attack Below the 0.5Mo Steel Curve in Figure A.1

Point	Temperature		Hydrogen Partial Pressure (Absolute)		Service Hours (Approximate)	Degrees Below 0.5Mo Curve (Approximate)	
	°F	°C	psi	MPa		°F	°C
36A [a]	790	421	350	2.41	80,000	20	11
37B [a]	800	427	285	1.97	57,000	30	17
38C [a]	640	338	270	1.86	83,000	180	100
39D [a]	700	371	300	2.07	96,000	125	69
41F [a]	760	404	375	2.59	85,000	40	22
42G [a]	750	399	350	2.41	150,000	60	33
43H [a]	625	329	350	2.41	150,000	185	103
44I [a]	730 [b]	388 [b]	313	2.16	116,000	90	50
45J [c]	620/640	327/338	457	3.15	70,000	167/147	93/82
46K [a]	626/680	330/360	350	2.41	131,000	184/130	102/72
47L [c]	684 [b]	362	738	5.09	61,000	54	30
48M [e]	550/570	288/299	1060/1100	7.31/7.59	79,000	125/105	69/58
[f]	655/670	346/354	—	—	17,500	20/5	11/3
49S [c]	750/770	399/410	390	2.69	67,000	50/30	28/17
[f]	650	343	—	—	163,000	150	83
51U [c]	690	366	397	2.74	—	100	56
53W [e]	545	285	2190	15.1	140,000	45	25
54AA [a]	725/760	385/404	300/380	2.07/2.62	105,000	40/100	22/56
55BB [a]	800/850	427/454	175/190	1.21/1.31	124,000	80/30	44/17
56CC [a]	810/825	432/441	275/300	1.90/2.07	223,000	15/0	8/0
57DD [a]	850 [d]	454 [d]	225 [d]	1.55 [d]	158,000	10	6
58EE [a]	810/855	432/457	170	1.17	138,000	70/25	39/14
59FF [c]	550/600	288/316	2000	13.79	210,000	50/0	28/0
60GG [c]	550/600	288/316	2000	13.79	210,000	50/0	28/0
61HH [c]	530/600	277/316	2200	15.17	210,000	60/0	33/0
62II [c]	670/700	354/371	190	1.31	192,000	180/150	100/83
63JJ [c]	600/750	316/399	500	3.45	235,000	180/30	100/17
64KK [c]	600/770	316/410	525	3.62	283,000	170/0	94/0
65LL [c]	775	413	550	3.79	—	0	0

NOTE Numbers and letters in the first column (labeled “Point”) refer to references and comments for Figure A.1.

Where two numbers are given, the first number represents average operating conditions while the second number represents maximum operating conditions.

[a] Catalytic reformer service.

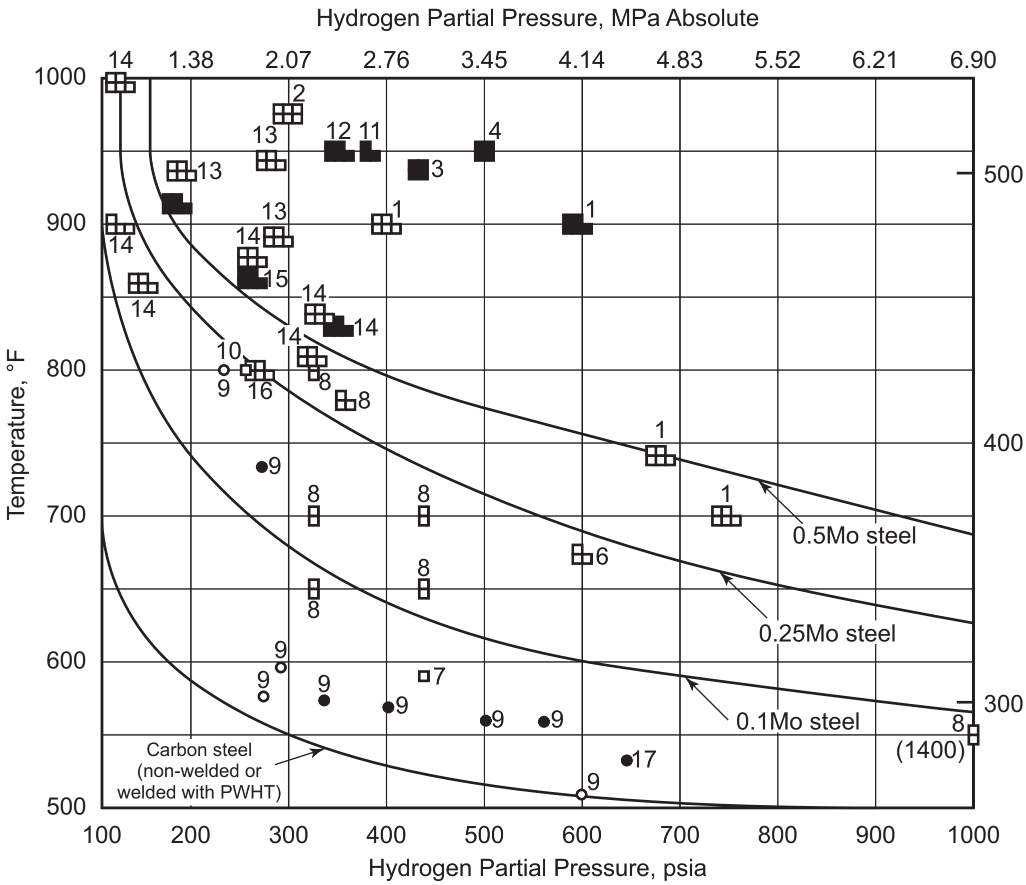
[b] Average.

[c] Hydrodesulfurizer service.

[d] Maximum.

[e] Ammonia plant.

[f] API task group currently resolving these points.



NOTE 1 Mo has four times the resistance of Cr to HTHA.

NOTE 2 Mo is equivalent to V, Ti, or Nb up to 0.1 %.

NOTE 3 Si, Ni, and Cu do not increase resistence.

NOTE 4 P and S decrease resistance.

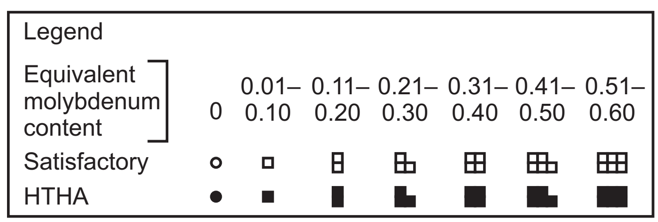


Figure A.2—Steels in High Temperature Hydrogen Service Showing Effect of Molybdenum and Trace Alloying Elements

A.4 References for Figure A.2

The data in Figure A.2 are labeled with the reference numbers corresponding to the sources listed in Table A.2.

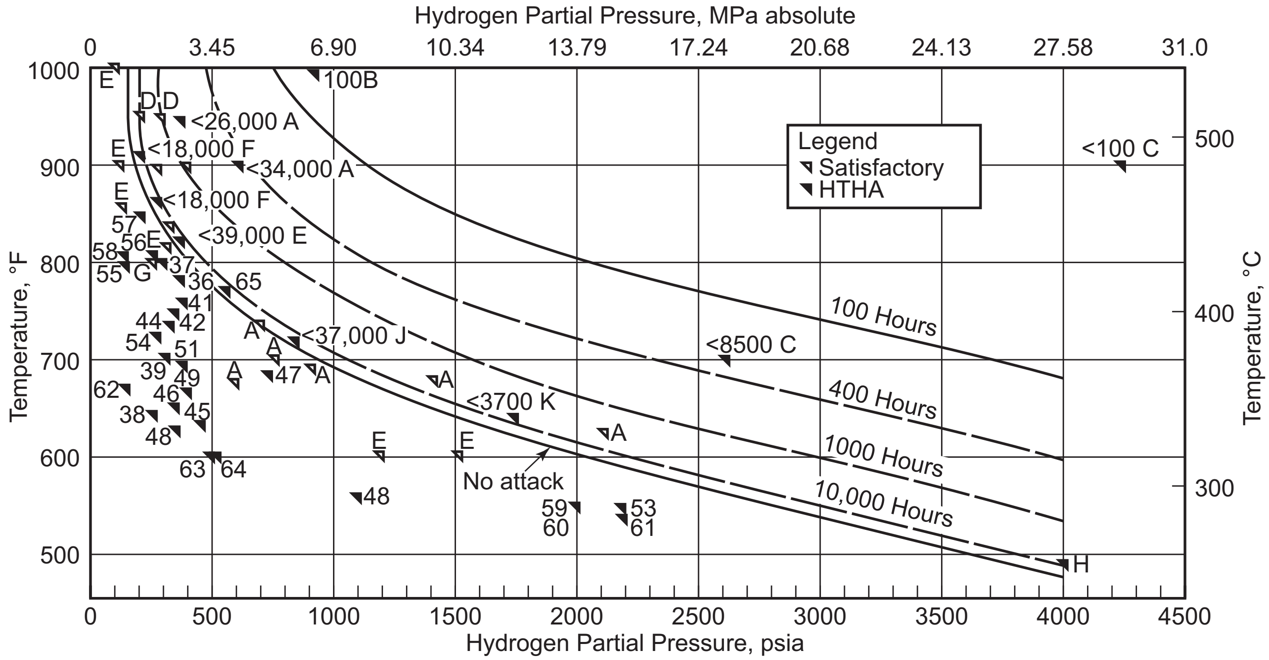


Figure A.3—Incubation Time for High Temperature Hydrogen Attack Damage of 0.5Mo Steels in High Temperature Hydrogen Service

Table A.2—References Along with Chromium, Molybdenum, Vanadium and Molybdenum Equivalent Values for Figure A.2

No.	Reference	Analysis			Mo Equiv.
		Cr	Mo	V	
1	Shell Oil Company [a]		0.50		0.50
2	Weld Deposits, D.J. Bergman [a]	0.79	0.39		0.59
3	Weld Deposits, D.J. Bergman [a]	0.80	0.15		0.35
4	Weld Deposits, D.J. Bergman [a]	0.50	0.25		0.37
5	Continental Oil Company [a]		0.25		0.25
6	Standard Oil Co. of California [a]		0.27		0.27
7	Standard Oil Co. of California [a]	0.05	0.06	0.08	
8	A.O. Smith Corp. [a]			0.13 to 0.18	0.11
9	Shell Development Co., Drawing No. VT 659-2				
10	Amoco Oil Company [a]	0.04			0.01
11	R.W. Manuel, Corrosion, *17*(9), pp. 103–104, Sept. 1961	0.27	0.15		0.22
12	The Standard Oil Co. of Ohio [a]	0.11	0.43		0.50
13	Exxon Corporation [a]				
14	Union Oil of California [a]				
15	Amoco Oil Company [a]				
16	Standard Oil Co. of California [a]				
17	Gulf Oil Corporation [a]				

[a] Private communication to Subcommittee on Corrosion (now Subcommittee on Corrosion and Materials).

Annex B
(informative)

HTHA of 1.25 Cr-0.5Mo Steel

The purpose of this annex is to provide a brief summary of the information and experience regarding three case histories with HTHA of 1.25Cr-0.5Mo steel.

Experiences with HTHA are listed in Table B.1 and the operating conditions are plotted in Figure B.1.

Table B.1—Experience with HTHA of 1.25Cr-0.5Mo Steel at Operating Conditions Below the Figure 1 Curve

Case	Temperature		Hydrogen Partial Pressure (Absolute)		Service Years	Description
	°F	°C	psi	MPa		
A	960	516	331	2.28	26	1.5 NPS Schedule 80 nozzle was broken off a catalytic reformer outlet line during a shutdown. Metallography indicated surface decarburization and intergranular cracking with bubbles. Cr content was 1.09 %.
B	977	525	354	2.44	14	Blistering was detected with ultrasonic examination in catalytic reformer piping. Metallography indicated surface decarburization and blistering at nonmetallic inclusions, with intergranular cracks growing from the blisters. Cr content was 1.10 %.
C	957/982	514/528	294/408	2.03/2.81	16	Blistering near pipe inner surface. Examination showed decarburization between the inner surface and the blister. Gas analysis indicated methane in the blister. Cr content was 1.12 %.
	See Note	See Note	See Note	See Note		

NOTE Average conditions are reported as the left number. Maximum condition reported as the right number.

Cases A and B were reported by Chiyoda Corporation in Japan. Case C was originally reported by Merrick and Maguire of Exxon [7]. The mechanisms of attack were similar in Cases B and C. That is, damage was in the form of internal blistering with decarburization and intergranular cracking from the edges of the blisters. In Case A, however, attack resulted in intergranular separation. All three steels had chromium contents near 1.1 %, near the 1.0 % lower limit for 1.25Cr-0.5Mo steels. Additionally, the Case A steel had a relatively high impurity content with an X-bar equal to 31.5, as defined by Bruscato [38].

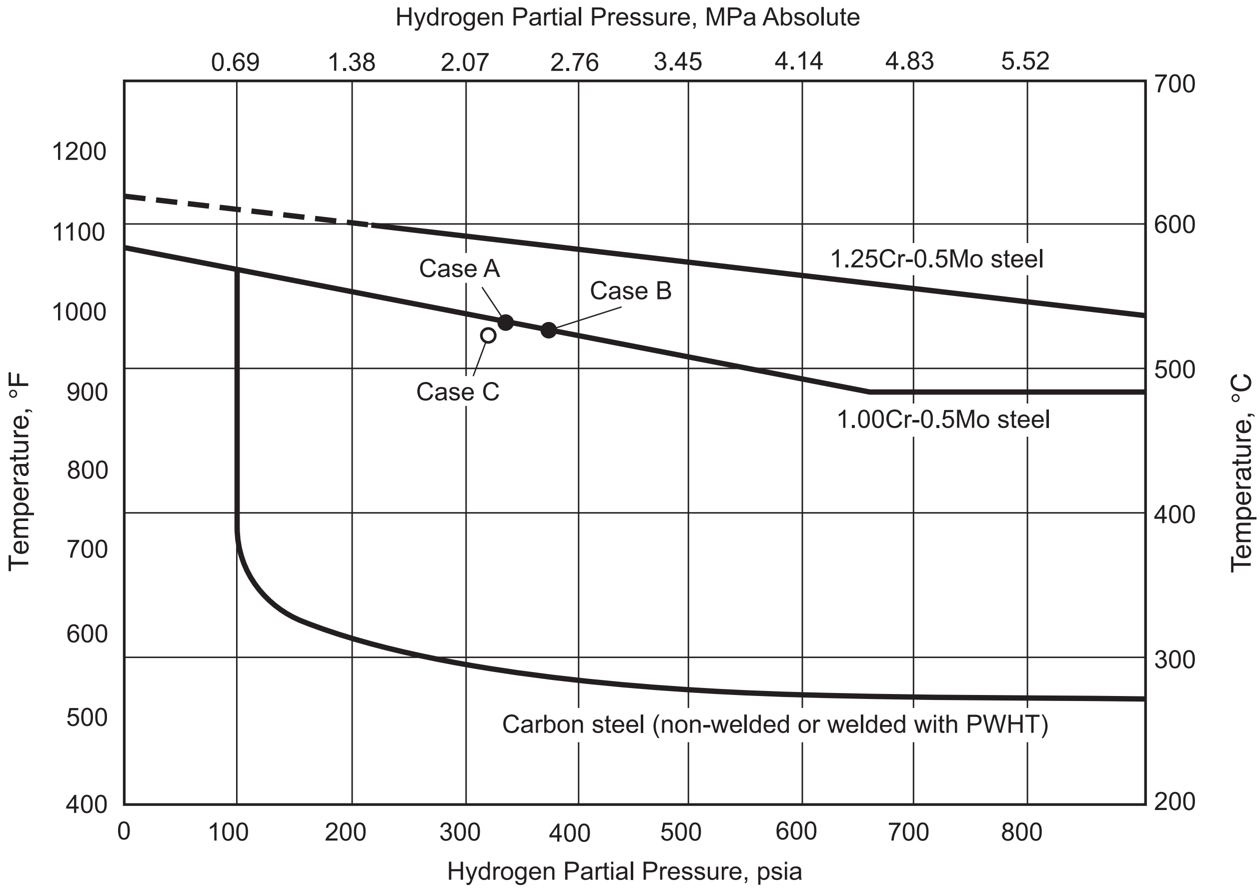


Figure B.1—Operating Conditions for 1.25Cr-0.5Mo Steels That Experienced High Temperature Hydrogen Attack Below the Figure 1 Curve

Annex C
(informative)

HTHA of 2.25Cr-1Mo Steel

The purpose of this annex is to provide a brief summary of experience regarding a case history [5] with HTHA of 2.25Cr-1Mo steel.

A recent experience with HTHA is described in Table C.1. This case history may indicate that highly stressed components can suffer HTHA at conditions below the curve in Figure 1. In this case history, a mixing tee was believed to be highly stressed by thermal stresses due to the mixing of hot and cooler hydrogen. Figure C.1 plots the operating conditions of both the hot upstream hydrogen and the mixed hydrogen downstream of the tee.

Table C.1—Experience with High Temperature Hydrogen Attack of 2.25Cr-1Mo Steel at Operating Conditions Below the Figure 1 Curve

Temperature		Hydrogen Partial Pressure (Absolute)		Time in Service Years	Description
°F	°C	psi	MPa		
675/820	357/438	1385/1570	9.54/10.82	>20	A mixing tee for the hot and cold makeup hydrogen to a hydroprocessing unit leaked near the weld to the downstream piping. SEM examination indicated decarburization and fissuring along the internal surface of the tee.
See Note	See Note	See Note	See Note		Although the leak path was not positively identified, it was concluded to be most likely due to fine, interconnected fissures. Some thermal fatigue cracking was also identified in the tee. Piping downstream of the tee was also found to have fissuring and internal decarburization to a depth of about 3.90 mils (0.1 mm) along the inside surface. The hot, upstream piping was not found to be attacked.

NOTE Average conditions are reported as first number. Maximum condition reported as second number.

[5] Communication to the API Subcommittee on Corrosion and Materials from Exxon Research and Engineering, August 1995.

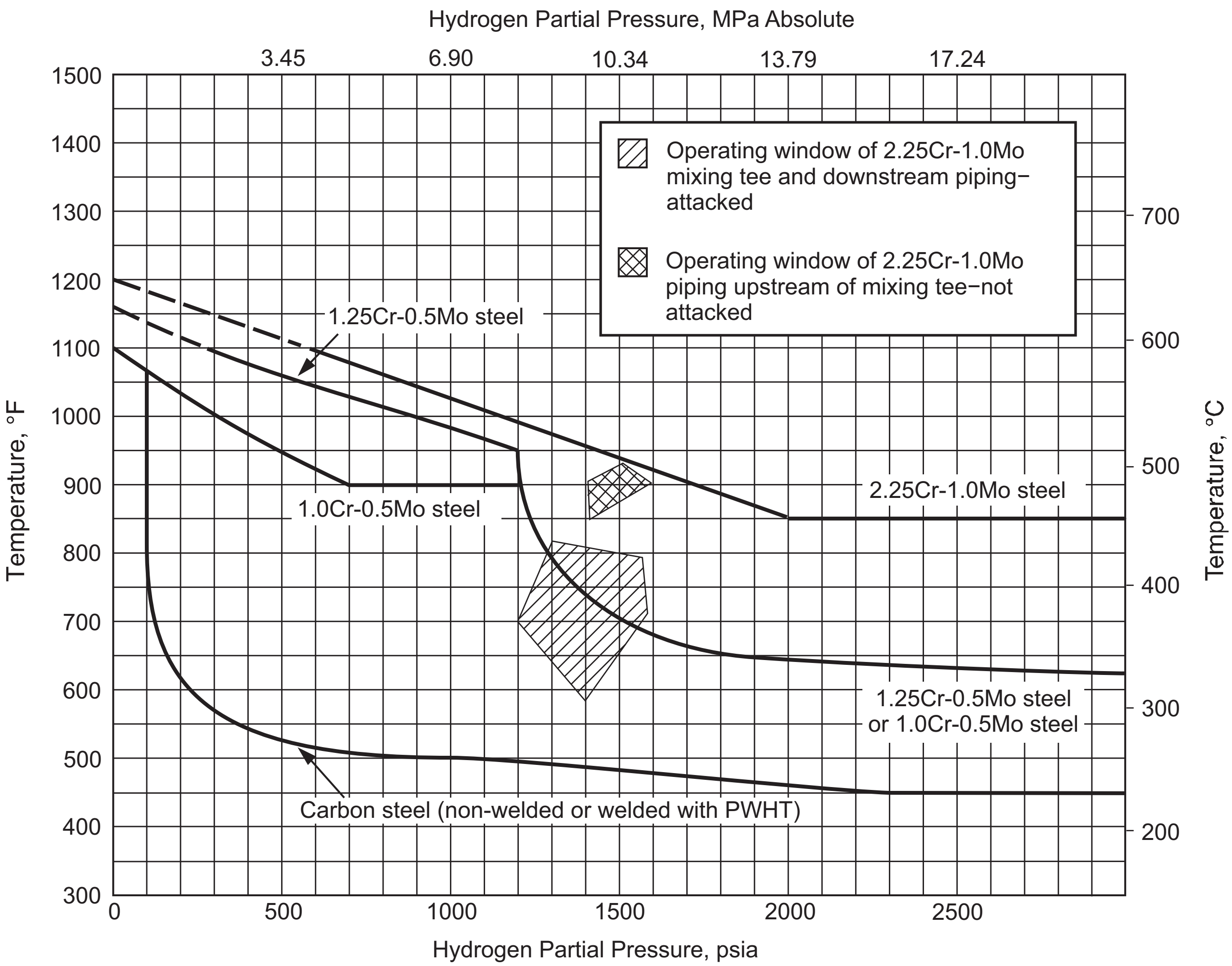


Figure C.1—Operating Conditions of 2.25Cr-1Mo Steels That Experienced High Temperature Hydrogen Attack Below the Figure 1 Curve

Annex D
(informative)

Effective Pressures of Hydrogen in Steel Covered by Clad/Overlay

The purpose of this annex is to provide a method for determining the effective pressure at the clad/overlay-to-base metal interface. More details and information (such as data for solubility and diffusivity for various alloys) can be obtained in the technical basis document [39].

Very low diffusivity of hydrogen in stainless clad or overlay materials used for corrosion protection results in an effective pressure of hydrogen at the clad/overlay-to-base metal interface (bond line) that is lower than that of the process stream. This effective pressure is calculated as follows.

$$C_{\mathrm{B,\ without\ clad}} = K_{\mathrm{B}}\sqrt{P_{\mathrm{H2}}} \tag{D.1}$$

The maximum steady state hydrogen concentration in the base metal without a stainless steel clad or overlay is given by:

$$C_{\mathrm{B,\ with\ clad}} = \frac{K_{\mathrm{C}}\sqrt{P_{\mathrm{H2}}}}{1+Z} \tag{D.2}$$

The maximum steady state hydrogen concentration in the base metal with a stainless steel clad or overlay is given by:

$$Z = \frac{D_{\mathrm{B}}X_{\mathrm{C}}K_{\mathrm{B}}}{D_{\mathrm{C}}X_{\mathrm{B}}K_{\mathrm{C}}} \tag{D.3}$$

The ratio of the of the hydrogen concentration in the base metal without and with a cladding is then given by:

$$R = \frac{C_{\mathrm{B,\ without\ clad}}}{C_{\mathrm{B,\ with\ clad}}} + \frac{1}{1+Z} \tag{D.4}$$

The effective hydrogen partial pressure for a wall with an intact clad or overlay is therefore given by:

$$P_{\mathrm{H2,\ effective}} = \frac{1}{(1+Z)^2} \tag{D.5}$$

where

P_{H2} is the hydrogen partial pressure in operating environment;

$P_{\mathrm{H2,\ effective}}$ is the effective hydrogen pressure at the clad/overlay-to-base metal interface;

D_{C}, D_{B} is the diffusivities of hydrogen in clad/overlay and base metal, respectively;

X_{C}, X_{B} is the thicknesses of clad/overlay and base metal, respectively;

K_{C}, K_{B} is the solubility of hydrogen in clad/overlay and base metal at 1 psi hydrogen partial pressure, respectively.

NOTE Terms are dependent on temperature and must be expressed in appropriate units.

Annex E
(informative)

Summary of Inspection Methods

Table E.1—Summary of Ultrasonic Inspection Methods for High Temperature Hydrogen Attack

	Ultrasonic Methods										
	Velocity Ratio	Attenuation	Spectral Analysis	Backscatter					Conventional Shear Wave UT and TOFD	High Frequency Shear Wave	Angle-beam Spectrum Analysis
				Amplitude Based	Pattern Recognition	Spatial Averaging	Directional Dependence	Frequency Dependence			
Description	Ratio of shear and longitudinal wave velocity is measured. HTHA changes the ratio.	Dispersion of ultrasonic shear wave is measured by recording drop in amplitude of multiple echoes. HTHA increases attenuation.	The first backwall signal is analyzed in terms of amplitude versus frequency. HTHA will attenuate high frequency response more than low frequencies.	High frequency ultrasonic waves backscattered from within the metal are measured. HTHA can increase backscatter signal amplitude.	High frequency ultrasonic waves backscattered from within the metal are analyzed. HTHA causes a rise and fall in backscatter pattern.	Backscatter data are collected over an area scanned. The signal is averaged to negate grain noise.	Compares backscatter signal as taken from ID and OD directions. HTHA damaged material will show a shift in indicated damage towards the exposed surface (ID).	Compares backscatter of two different frequency transducers. HTHA damaged material will show a shift and spread of backscatter in time.	Routinely used for crack detection at weldments. Higher frequencies increase detection capability. TOFD is a developing technology.	High frequency (10 MHz or higher) shear waves operated in pulse-echo mode for detection of HTHA in weldments/ HAZ. Requires use of focused beam to inspect thick vessels.	The spectrum of any suspect signal from pulse-echo inspection of weld/HAZ is compared with a reference spectrum taken in the pitch-catch mode from the base metal. HTHA causes the pulse-echo spectrum to increase amplitude with increase of frequency.
Detection capability	Has been shown to detect HTHA fissures in base metal away from weldments. Can differentiate between HTHA damage and plate laminations.	Has been shown to detect HTHA fissures in base metal away from weldments.	Has been shown to detect HTHA fissures in base metal away from weldments.	Has been shown to detect HTHA fissures in base metal away from weldments.	Has been shown to detect HTHA fissures in base metal and weld metal.	Has been shown to detect HTHA fissures in base metal and weld metal.	Has been shown to detect HTHA fissures in base metal and weld metal.	Has been shown to detect HTHA fissures in base metal and weld metal.	Can reliably detect HTHA only after cracks have formed. Cannot detect HTHA fissures.	Has been shown to detect HTHA fissures in weld HAZ.	Has been shown to detect HTHA fissures in weld HAZ.
Advantages	Not affected by inclusions, grain size, or surface roughness, or curvature. No prior inspection history needed for interpretation.	Simple to use.	Very sensitive to internal fissuring due to HTHA. Can be used to differentiate between inclusions and HTHA damage.	Very sensitive to internal fissuring due to HTHA. Can be used for scanning. Can give an indication of depth of HTHA. Can be automated in either a B-scan or C-scan mode. Can be used to monitor changes in extent of damage.	Very sensitive to internal fissuring due to HTHA. Can be used for scanning. Can give an indication of depth of HTHA. Can differentiate between HTHA damage and inclusions.	Sensitive to internal fissuring due to HTHA. Can be used to improve detection of fissuring stages of HTHA and to determine depth of damage.	Very sensitive to internal fissuring due to HTHA. Can be used to differentiate between HTHA damage and other internal defects such as inclusions.	Very sensitive to internal fissuring due to HTHA. Can be used to differentiate between HTHA damage and other internal defects such as inclusions.	Can scan full coverage of weldments from the OD.	Can scan full coverage of weldments from the OD. Very sensitive to internal fissuring due to HTHA. Can be used to differentiate between HTHA damage and welding defects and inclusions. Can be used for scanning. Can give an indication of depth of HTHA. Can be automated in either a B-scan or C-scan mode. Can be used to monitor changes in extent of damage.	Can scan full coverage of weldments from the OD. Very sensitive to internal fissuring due to HTHA. Can be used to differentiate between HTHA damage and welding defects and inclusions.

Table E.1—Summary of Ultrasonic Inspection Methods for High Temperature Hydrogen Attack (Continued)

	Ultrasonic Methods										
				Backscatter							
	Velocity Ratio	Attenuation	Spectral Analysis	Amplitude Based	Pattern Recognition	Spatial Averaging	Directional Dependence	Frequency Dependence	Conventional Shear Wave UT and TOFD	High Frequency Shear Wave	Angle-beam Spectrum Analysis
Limitations	Covers only local spot where probe is held. Cannot be used for scanning large areas. Cannot detect HTHA damage that is less than 10 % through wall. Cladding can cause false interpretation if included in velocity measurement.	Covers only local spot where probe is held. Cannot be used for scanning. ID or OD surface corrosion can give false readings. Needs parallel surfaces. Thick materials decrease sensitivity. Difficult to get similar repeat readings when used as a monitoring program.	Technique is best when used as a comparison of a clean non-HTHA area versus a suspect area.	Inclusions, large grains, ID pitting, laminar defects, or scale can give false indications of HTHA. Damage from HTHA attenuates backscatter signal, which can cause false interpretations in sizing and characterizing the flaw.		Not a primary method, usually a complementary method.	Requires access to both ID and OD surfaces. Does not work well on clad equipment.	Not a primary method, usually a complementary method. Does not work well on very shallow HTHA damage.	Cannot detect HTHA fissures. Can only detect HTHA cracks. Actual crack sizing can be difficult.	Accurately sizing the depth of HTHA fissures in weld HAZ may be difficult.	
Recommendations	Recommended for base metal HTHA detection when 1) advanced HTHA damage is suggested by the results of other methods or 2) used as a complementary technique with a backscatter method.	Not recommended for HTHA inspection.	Used as a complementary technique after backscatter method indicates possible damage.	Recommended only when used with other techniques. Should be limited to the initial screening.	Recommended only when used with other techniques as the first step of inspection.	Used as a complementary technique when depth of damage cannot be clearly identified.	Used as a complementary technique after backscatter pattern recognition technique indicates possible damage.	Used as a complementary technique after backscatter pattern recognition technique indicates possible damage.	Not recommended for HTHA inspection to detect fissures. Can be used to detect developed cracks.	Recommended for detection and sizing of localized HTHA in weld/HAZ.	Recommended as a complementary technique after high frequency shear wave indicates possible damage.

Table E.2—Summary of Non-ultrasonic Inspection Methods for High Temperature Hydrogen Attack

	Other Methods				
	Magnetic Particle	**Field Metallography and Replication**	**Radiography**	**Visual**	**Acoustic Emission**
Description	Conventional wet fluorescent AC yoke magnetic particle inspection used for detection of cracks at a surface. Blending the welds and sanding smooth increases sensitivity.	Polish and etch as in a creep evaluation looking for fissures, possibly voids, and changes in microstructure, i.e. decarburization. Replicas can be taken for laboratory analysis.	Conventional radiography used to inspect welds for cracks.	Internal visual inspection of pressure vessels for surface blistering.	Monitors the sound that cracks emit when they are stressed.
Detection capability	Can detect HTHA only after cracks have formed. Cannot detect fissures or voids.	Can differentiate between HTHA damage (fissures and decarburization) and other forms of cracking. Detailed field metallography may detect voids, but this performance level should be demonstrated before relied upon by the user.	Can detect HTHA only after cracks have formed. Cannot detect fissures or voids.	Blisters are readily apparent when present. However, HTHA may frequently occur without the formation of surface blisters.	Reported to be capable of detecting cracks. Currently not known whether fissures can be detected.
Advantages	Crack indications can be seen visually and little interpretation is required.	Only nondestructive confirmation method. Can be used at welds and base metal.	Radiographic film gives a record of detected cracks. Additionally, radiography can sometimes be used for crack detection without insulation removal, although sensitivity with insulation in place may be poor.	No special inspection tools are needed. Blister interpretation is clear.	Capability for monitoring a large system including piping and pressure vessels. Potentially offers a technique for identifying areas needing follow-up inspection. May offer a method for full coverage of base metal.
Limitations	Cannot detect HTHA fissures or voids. Detects only the advanced stages after cracks have already formed. Only detects surface cracks. Exam is performed from the ID. Cannot determine the depth of HTHA damage.	Cladding must be removed if present. Best if $^1/_{16}$ in. to $^1/_8$ in. (2 mm to 3 mm) of material is removed to reveal subsurface damage. Cannot nondestructively determine the depth of HTHA damage.	Cannot detect the fissure stages of HTHA. May miss cracks, depending upon the orientation of the crack plane.	HTHA frequently occurs without the formation of surface blisters. Blisters, when present, are likely to be an indication of advanced HTHA. Cracking is not always visible.	Not a proven technique for HTHA detection. Needs an applied stress during the test, usually by hydrostatic testing. Another test method uses thermal stress during equipment cooldown.
Recommendations	Recommended for internal inspection of pressure vessels to use in addition to UT techniques, recognizing it is limited to advanced stages of HTHA with cracking. It will not find fissures.	Can be used to follow-up on indications from other methods or in suspected damage areas.	Not recommended for general HTHA detection. May be useful for verification of shear wave UT indications.	Recommended for internal inspection of pressure vessels to use in addition to UT and MT techniques.	Additional development work and field trials recommended. Not currently recommended as a primary method for HTHA detection.

Annex F
(informative)

HTHA of Non-PWHT'd Carbon Steels

F.1 General

The purpose of this annex is to provide a brief summary of the information and experience regarding the use of welded, but not PWHT'd, carbon steels in elevated temperature and pressure hydrogen service.

In the fall of 2011 API issued an alert to inform users that there have been several reports of cracking-related issues with carbon steel piping and equipment in high temperature, high pressure hydroprocessing service at operating conditions where carbon steel was previously thought to be resistant to HTHA. Some companies no longer specify non-PWHT'd steel for new or replacement equipment used for operation up to the earlier carbon steel curve in Figure 1 because of the uncertainties regarding its performance after prolonged use. Since the year 2000, a series of unfavorable service experiences has reduced confidence in the position of the carbon steel curve for non-PWHT'd components [34].

In the Eighth Edition (2015) of this publication, a new welded carbon steel, but not PWHT'd, curve was introduced positioned at 400 °F (204 °C) from about 2200 psia (15.17 MPa) to 13,000 psia (89.63 MPa), then approximately 50 °F (28 °C) lower than the 1977 edition, from about 900 psia (6.21 MPa) to 2200 psia (15.17 MPa), then widening its separation with the non-welded or PWHT'd carbon steel curve to a maximum slightly higher than about 100 °F (56 °C) at the curve elbow to finally turn vertical at 50 psia (0.34 MPa). The past carbon steel curve will continue to be used to represent carbon steel components that are not welded or welded and PWHT'd. Plant experience has identified 12 new instances of HTHA or cracking of welded, but not PWHT'd carbon steel below the 1977 curve. The operating conditions for these instances are given in F.2 for Figure F.1 and are plotted on Figure F.1.

Prior to these recent reports, the only reported failures of carbon steel below the API RP 941, Figure 1 curve were in cases of exceptionally high stress, as discussed in 5.2 and 5.3. All of the new reports of HTHA involve carbon steel equipment that was not PWHT'd after welding during fabrication. Past research summarized in API TR 941, *The Technical Basis Document for API RP 941*, states that non-PWHT'd welds not only retain high residual welding stresses, but also have lower carbide stability in the weld HAZ that further increases HTHA susceptibility.

Existing equipment with non-PWHT'd welded carbon steel that is operated above the new non-PWHT'd welded carbon steel curve in Figure 1 should be evaluated in regards to HTHA risk. Owners/operators may choose to replace such equipment or prioritize such equipment operating above the new curve for inspection. Plant experience suggests that important variables to consider in prioritizing equipment for inspection include severity of operating condition (hydrogen partial pressure and temperature), thermal history of the steel during fabrication, stress, cold work, and cladding composition and thickness, when present.

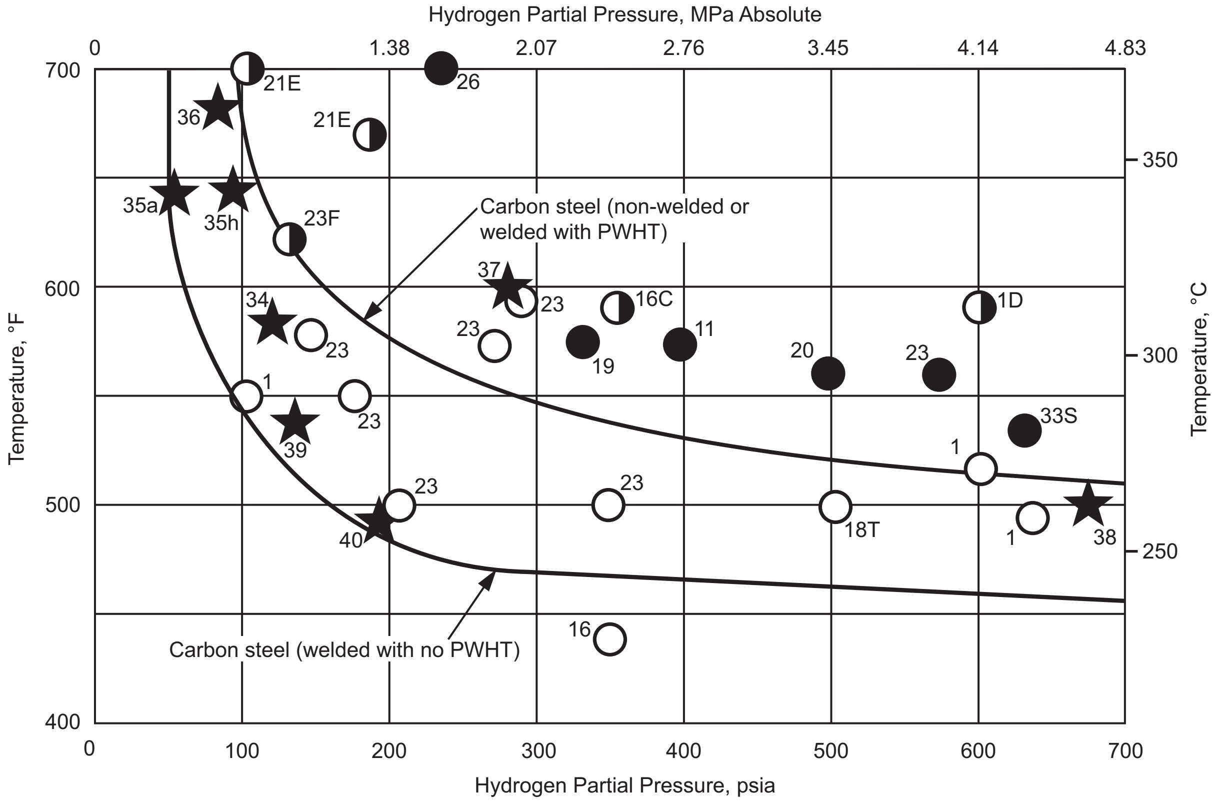
Owners/operators should add a safety factor even to the new Figure F.1 curve, because operations just below the curve may still be at-risk due to issues such as discrepancies in temperature measurement, fouling of heat transfer surfaces, and temperature excursions.

F.2 References and Comments for Figure F.1

F.2.1 References

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.



NOTE This Figure is adapted from Figure 1, Eighth Edition (2015) of this publication. Numbered and lettered references for point in this figure refer to data listed in 3.5 and F.2.

Figure F.1—Operating Conditions for Carbon Steel (Welded with No PWHT) That Experienced HTHA Below the 1977 Carbon Steel Figure 1 Curve

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.

F.2.2 Comments

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 and at 125 psia.

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 welds in gasoline hydrotreating service. One cracked on the pipe side of the pipe-to-flange weld. Operating at 645 °F (340 °C) and 57 psia to 94 psia (0.39 MPa to 0.65 MPa) hydrogen partial pressure.

X) Point 37. After 14 years, 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 and at 280 psia.

Y) Point 36. After 6 years, multiple non-PWHT'd carbon steel flanges cracked in the HAZs on the flange side of flange to pipe welds in a gasoline desulfurization unit. Operating at roughly 670 °F and at 85 psia.

Z) Point 38. After 29 years, non-PWHT'd carbon steel exchanger shell in HDS service cracked. Operating at roughly 500 °F and at 670 psia.

A.1) Point 39. After 10 years, inspection found cracks in non-PWHT'd carbon steel exchanger shell in light hydrotreater service. Operating at roughly 540 °F and at 130 psia.

B.1) Point 40. After 30+ years, inspection found cracks in non-PWHT'd carbon steel exchanger shell in light hydrotreater service. Operating at roughly 490 °F and at 195 psia.

F.3 References

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.

Chemical Safety Board draft report titled "Draft Report 2010-08-I-WA, Tesoro Anacortes Refinery."

D. Miller, API letter to The Honorable Rafael Moure-Eraso of the CSB, dated March 14, 2014, titled "Draft Report 2010-08-I-WA, Tesoro Anacortes Refinery."

Annex G
(informative)

Methodology for Calculating Hydrogen Partial Pressure in Liquid-filled Piping

G.1 General

This annex addresses the issue of calculating the hydrogen partial pressure to be applied to Figure 1 for liquid only or liquid-filled systems, where the liquid contains dissolved hydrogen, but there is no separate vapor phase present, both with and without downstream increases in total pressure. The RP is to use the hydrogen partial pressure of the vapor that was last in equilibrium with the liquid in question, or the calculated hydrogen partial pressure that would be in equilibrium with the liquid at its operating temperature and pressure. Prior to the Eighth Edition of this RP, it did not address the issue of a liquid containing dissolved hydrogen that is pumped to a pressure above its bubble point. For such a liquid, there is no "co-existing" vapor to examine for hydrogen partial pressure; however, the dissolved hydrogen in the liquid can lead to HTHA.

Examples of liquid-filled lines containing hydrogen include hydroprocessing unit separator liquid lines (upstream of pressure let-down valves), some hydroprocessing unit feed lines and equipment (when hydrogen is injected as a soak gas and then is completely absorbed by the liquid as the temperature increases), gasoline desulfurization units with pumping of the reactor bottoms streams, some biofuel units, some coal liquefaction units, and some gasification units.

Operating companies observed piping failure in pressurized liquid services containing dissolved hydrogen where the piping was thought to be in compliance with this RP. This annex contains five proposed methods to enable engineers to use this RP for pressurized liquid services.

The five methods are as follows.

— *Conventional Thermodynamics*

1) The partial pressure of dissolved gaseous species is generally defined as the partial pressure of the dissolved species (in vapor) in equilibrium with the liquid at the same temperature (i.e. the partial pressure downstream of the pumps is assumed to be very close to the partial pressure upstream). Process modeling experts report that this should be very close to the actual value (within 5 %).

2) This is consistent with the previous API 941 guidance and is appropriate for liquid lines from vessels down to pumps.

— *Total Pressure Method*

1) Start with the pressurized liquid and reduce the pressure to the bubble point. Calculate the hydrogen mole fraction of the incipient vapor.

2) Determine the pressurized liquid effective ppH_2 by multiplying that mole fraction by the total (absolute) pressure of the pressurized liquid.

For liquids that are pumped from bubble point to some higher pressure, the practitioner can simply start with the known equilibrium vapor phase properties, prior to pumping.

The other possible calculation methods are as follows:

— Pure Hydrogen Equivalency Method,

— Fugacity Correction Method, and

— Composition Variation and Compensation Method.

These tend to give results within 5 % of the Conventional Thermodynamics Method.

— *Pure Hydrogen Equivalency Method*

1) Using an appropriate thermodynamic method, calculate the fugacity of hydrogen in the liquid phase. Actual temperature and pressure should be used.

2) Find the pressure of a pure hydrogen stream (at the same temperature) such that the hydrogen fugacity is the same. The resulting pure hydrogen pressure (absolute) is the effective ppH_2 of the stream in question.

The hydrogen equivalency method finds the pure hydrogen pressure that would have the same HTHA propensity as the subject pressurized stream with dissolved hydrogen. Since the Nelson curves are drawn with ppH_2 as the independent variable, this method will often result in a higher HTHA propensity (effective ppH_2) than the simple ppH_2 would indicate.

— *Fugacity Correction Method*

1) Start with the pressurized liquid and reduce the pressure to the bubble point. Calculate the hydrogen fugacity (it will be the same for both phases) and ppH_2 for the equilibrium vapor phase.

2) Calculate the hydrogen fugacity in the liquid after pressurization.

3) The ratio of the hydrogen fugacity at higher pressure to the hydrogen fugacity at the lower pressure equilibrium is the fugacity correction factor.

4) To find the effective ppH_2 for the high pressure liquid, multiply the equilibrium vapor phase ppH_2 by the correction factor.

For liquids that are pumped from bubble point to some higher pressure, the practitioner can simply start with the known vapor phase ppH_2 prior to pumping and apply the correction factor to account for the pressure increase.

This method rigorously corrects for the increase in HTHA propensity, while maintaining consistency with the data in this RP.

— *Composition Variation + Compensation Method*

1) Again start with a pressurized liquid and appropriate thermodynamic model.

2) Hold state and compositional variables constant, then add hydrogen until the sub-cooled liquid reaches the bubble point.

3) The pseudo-saturation H_2 partial pressure is determined.

4) This pseudo-saturation value is multiplied by the ratio of actual H_2 in the sub-cooled liquid to compensate for the H_2 addition, thus arriving at the sought after effective H_2 partial pressure.

G.2 Example 1 Showing the Total Pressure Method, the H_2 Equivalency Method, and the Fugacity Correction Method

The sketch below shows a typical example analysis. A narrow boiling range heavy cat naphtha (HCN) is drawn from a high pressure separator operating at 650 °F, 295 psig, and 124 psia ppH_2. The hydrocarbon liquid has a boiling range of 384 °F to 443 °F (by ASTM D86 Method for Distillation of Petroleum Products). The pump increases the pressure by 100 psi.

Table G.1 shows the effective hydrogen partial pressures for the streams before and after the pump (A and B) using the three methods.

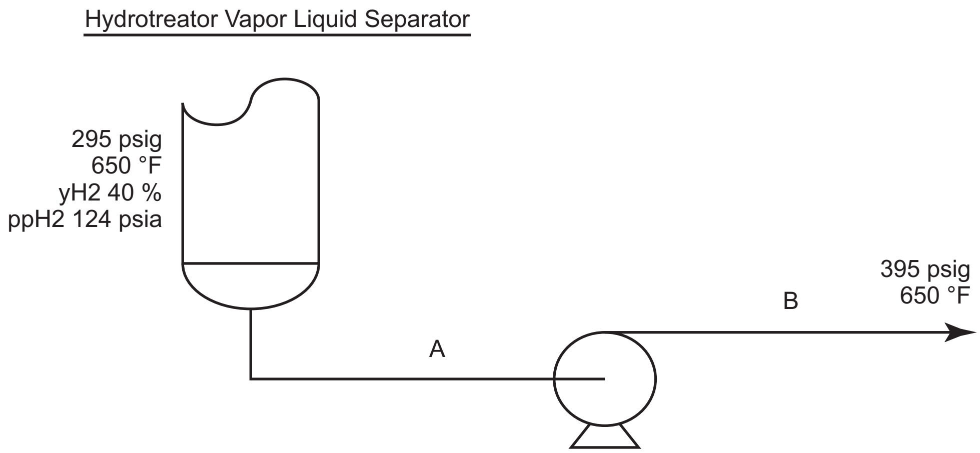


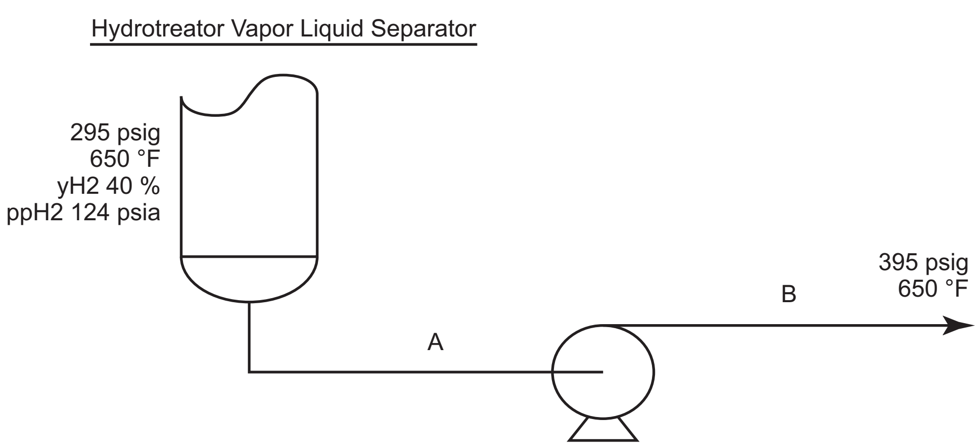
Table G.1—Effective Hydrogen Partial Pressures

All values are psia

Calculation Method	Effective ppH_2 at A	Effective ppH_2 at B
Previous edition of API RP 941 (Conventional Thermodynamics)	124	164
Total Pressure Method	124	164
Pure H_2 Equivalency	153 (Note)	162
Fugacity Correction Method (factor = 1.0595)	124	131

NOTE With the Pure Hydrogen Equivalency Method, the dissolved hydrogen before the pump has the same fugacity (chemical potential and activity) as pure hydrogen at 153 psia (for 650 °F). This is a higher value than the 124 psia ppH_2 as calculated using API RP 941.

G.3 Example 2 Showing the Methods in Example 1 with the Composition Variation + Compensation Method



- Simulate a separator with a H_2-Cetane (n-C16) liquid packed line at 550 °F, 650 psia. The hydrogen molar percentage at the separator is 97.5 % with a H_2 pp of 633.6 psia. The new conditions at point B are 550 °F and 800 psia.
- H_2-Cetane system is an idealization of a diesel hydrotreater.
- Bottoms of separator taken through a pump with a pressure differential of 150 psi.
- The H_2 partial pressure determined at the discharge using the various methods described above is presented in Table G.2.

Table G.2—Effective Hydrogen Partial Pressures with the Composition Variation + Compensation Method

	Thermodynamic Definition	Total Pressure	Hydrogen Equivalency	Fugacity Correction Factor	Composition Variation + Compensation
H_2 pp	633.6	779.8	646.1	620.1	630.1
% difference	0.0	23.1	2.0	2.1	0.6
Effective H_2 pp at this location	A	B	B	B	B

G.4 References

P66 Technical Memorandum titled “Estimating Hydrogen Attack Potential for Pressurized Liquids Containing Dissolved Hydrogen,” from Mitch Loescher, dated Sept. 1, 2011

“Methods for Approximating H_2 Partial Pressure in Subcooled Liquids,” presented at NACE CTW, Sept. 17, 2012, by Cathy Shargay, Alex Cuevas, Paul Mathias, and Garry Jacobs of Fluor.

Annex H
(informative)

Internal Company Data Collection

Request for New Information

The API Subcommittee on Corrosion and Materials collects data on the alloys shown in all figures or similar alloys that may come into use. Revisions to the curves will be published as the need arises.

For the existing curves, data are desired for instances of HTHA damage that occur above or below the curve for the steel involved; data are also desired for successful experience in the area above the curve for the steel involved. For chromium-molybdenum steels not included on the existing figures, data for successes and HTHA damage in any meaningful area are desired.

The following datasheet is provided for the reader's convenience in submitting new data. Available data should be furnished by inserting information in the spaces provided and checking the appropriate answer where a selection is indicated. Any additional information should be attached.

While both hydrogen partial pressure and temperature are important, particular attention should be given to obtaining the best estimate of accurate metal temperature. One method of obtaining more accurate data for a specific area is to attach a skin thermocouple to the area that previously exhibited high temperature hydrogen damage.

The completed form should be returned to the following address:

American Petroleum Institute
API Standards Department
1220 L Street, NW
Washington, DC 20005

Datasheet for Reporting High Temperature Hydrogen Attack (HTHA) of Carbon and Low-alloy Steels

Date ______________________________________ File No. ___________________________

By ____
(Name, Company, Address)

1. (a) ASTM specification (or equivalent) for the steel: ____

   (b) Design Code___________________________ _________

2. (a) Composition of steel (wt%) Fe ________ Cr________ Mo _________ V ________ Ni ________ P________ Sn ___________

   Ti _________ Nb _______ C __________ Si ________ Mn________ S________ As ___________

   (b) Steel protection: None __________________ Weld overlay material _________________________ Sb ___________

   Cladding material _______ Other _______________

   (c) Thickness Base metals _________ Weld overlay or cladding (if any) __________________________________

3. Heat treatment: Postweld heat treatment Yes ______ No ______ Temperature/Time _________________ °F/hr

   Normalized and tempered Yes ______ No ______ Tempering Temperature ______________ °F

   Quenched and tempered Yes ______ No ______ Tempering Temperature ______________ °F

   Other ____

4. Mechanical properties (prior to exposure): Yield strength (actual) _____________________ psi

   Ultimate strength (actual) __________________ psi

5. Temperature: Process: Average __________ °F Maximum ____________ °F

   Metal: Average __________ °F Maximum ____________ °F

6. Hydrogen partial pressure: ________________ psia (Describe method) Hydrogen purity _________________ %

7. Calculated operating stress: ________________ psi

8. Microhardness: For a failure, at or near crack: ____________________

   For successes: Weld: _______________ Base material ________________________

   Heat-affected zone: _______________________

9. Days in service: Total ___________________________ At maximum temperature __________________________

10. Damage Appearance Surface decarburization Yes ______ No ______ Surface cracking Yes ______ No ______

    Internal decarburization Yes ______ No ______ Internal fissuring Yes ______ No ______

    Blisters Yes ______ No ______ Isolated Blisters Yes ______ No ______

    Voids Yes ______ No ______

11. Location of failure (include photograph): Weld metal Yes______ No______ Heat-affected zone Yes______ No______

    Base material Yes______ No______

    Other ____

12. The type of process unit involved ____

13. Type of equipment (piping, vessels, heat exchanger, etc.) ____

14. Submit a photomicrograph showing typical failure and grain structure. Include 100X and 500X photomicrographs, plus any other appropriate magnifications. Attach any reports, if available. Please note any unusual circumstances.

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