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

API RECOMMENDED PRACTICE 941
SIXTH EDITION, MARCH 2004

American
Petroleum
Institute

Helping You
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Downstream Segment

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

0 Introduction

This recommended practice discusses the resistance of steels to high temperature hydrogen attack (HTHA). 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, Forms of High Temperature Hydrogen Attack, hydrogen reacts with the carbon in the steel to cause either surface decarburization or internal decarburization and fissuring, and eventually cracking. This form of hydrogen damage is called high temperature hydrogen attack.

1 Scope

This recommended practice 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 treating, chemical composition, and cladding are discussed. This recommended practice 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 recommended practice 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 recommended practice can also be applied to hydrogenation plants such as those that manufacture ammonia, methanol, edible oils, and higher alcohols.

Hydrogenation processes usually require standards and materials that may not be warranted in other operations of the petroleum industry. At certain combinations of elevated temperature and hydrogen partial pressure, both chemical and metallurgical changes occur in carbon steel, which in advanced stages can render it unsuitable for safe operation. Alloy steels containing chromium and molybdenum can be used under such conditions.

The steels discussed in this recommended practice resist 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 operating in the high temperature hydrogen attack range. This recommended practice 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 recommended practice will discuss in detail only the resistance of steels to high temperature hydrogen attack.

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

2 References

2.1 STANDARDS

Unless otherwise specified, the most recent editions or revisions of the following codes shall, to the extent specified herein, form a part of this publication.

ASME[1]

Boiler and Pressure Vessel Code

Section II, "Materials" (Part A, "Ferrous Material Specifications," and Part D, "Properties"),

Section III, "Rules for Construction of Nuclear Power Plant Components," and Section VIII, "Pressure Vessels," Divisions 1 and 2.

Code for Pressure Piping

ASME B31.3, "Chemical Plant and Petroleum Refinery Piping"

[1]ASME International, 3 Park Avenue, New York, NY 10016-0518, www.asme.org.

2.2 OTHER REFERENCES

In addition, this publication draws upon the work referenced in the following publications:

1. G. A. Nelson, "Hydrogenation Plant Steels," *Proceedings*, 1949, Volume 29M, American Petroleum Institute, Washington, D.C., pp. 163 – 174.

2. W. A. Pennington, *Transactions of the American Society for Metals,* 1946, Volume 37.

3. E. E. Fletcher and A. R Elsea, *Defense Metals Information Center Report 202*, Battelle Memorial Institute, Columbus, Ohio, 1964

4. API Publication 945, *A Study of the Effects of High Temperature, High-Pressure Hydrogen on Low-Alloy Steels,* American Petroleum Institute, Washington, D.C., 1975 (out of print).

5. F. K. Naumann, "Influence of Alloy Additions to Steel upon Resistance to Hydrogen Under High Pressure," *Technische Mitteilungen Krupp,* Volume 1, Number 12, 1938, pp. 223 – 234.

6. API Publication 940, *Steel Deterioration in Hydrogen,* American Petroleum Institute, Washington, D.C., 1967 (out of print).

7. R. D. Merrick and C. J. Maguire, "Methane Blistering of Equipment in High Temperature Service," *Paper No. 30* presented at the annual meeting of the National Association of Corrosion Engineers, March 1979.

8. I. Class, "Present State of Knowledge in Respect to the Properties of Steels Resistant to Hydrogen Under Pressure," *Stahl und Eisen,* Volume 80, pp. 1117 – 1135.

9. R. P. Jewett, "Effect of Gaseous Hydrogen on the Mechanical Properties of Metals Used in the Petroleum Industry," 1979 Proceedings-Refining Department, Volume 58, American Petroleum Institute, Washington, D.C., pp. 151 – 160.

10. T. Nomura, K. Murayama, and M. Matsushita, "Sample Test Results of All Liquid Phase Hydrogen Attack," Japan Energy Corporation, presented to the API Task Group on Hydrogen Deterioration of Steels, May 1994.

11. F. H. Vitovec, "The Growth Rate of Fissures During Hydrogen Attack of Steels," *Proceedings*, 1964, Volume 44, American Petroleum Institute, Washington, D.C., pp. 179 – 188.

12. G. Sundararajan and P. Shewmon, *Met. Trans A,* V12A, 1981, pp. 1761 – 1765.

13. B. L. Chao, G. R. Odette, and G. E. Lucas, "Kinetics and Mechanisms of Hydrogen Attack in 2.25Cr-1Mo Steel," *ORNL*/Sub/82-22276/01, August 1988.

14. G. A. Nelson, "Operating Limits and Incubation Times for Steels in Hydrogen Service," *Proceedings*, 1965, Volume 45, American Petroleum Institute, Washington, D.C., pp. 190 – 195.

15. R. D. Merrick and A. R. Ciuffreda, "Hydrogen Attack of Carbon – 0.5Molybdenum Steels," 1982 Proceedings, Refining Department, Volume 61, American Petroleum Institute, Washington, D.C., pp. 101 – 114.

16. M. G . Maggard, "Detecting Internal Hydrogen Attack," *Oil and Gas Journal,* March 10, 1980, pp. 90 – 94.

17. K. Ishii, K. Maeda, R. Chiba, and K. Ohnishi, "Intergranular Cracking of C-0.5Mo Steel in a Hydrogen Environment at Elevated Temperatures and Pressures," 1984 Proceedings, Refining Department, Volume 63, American Petroleum Institute, Washington, D.C., pp. 55 – 64.

18. R. Chiba, K. Ohnishi, K. Ishii, and K. Maeda, "Effect of Heat Treatment on the Resistance of C-0.5Mo Steel Base Metal and Its Welds to Hydrogen Attack," 1985 Proceedings, Refining Department, Volume 64, American Petroleum Institute, Washington, D.C., pp. 57 – 74.

19. M. Prager, "Hydrogen Attack Susceptibility Of Chrome-Moly Steels And Weldments," PVP Vol. 239/MPC Vol. 33, *Serviceability of Petroleum, Process, and Power Equipment,* American Society of Mechanical Engineers, New York, 1992.

20. E. A. Sticha, "Tubular Stress-Rupture Testing of Chromium-Molybdenum Steels with High-Pressure Hydrogen," *Journal of Basic Engineering*, December 1969, Volume 91, American Society of Mechanical Engineers, New York, pp. 590 – 592.

21. E. B. Norris and E. A. Sticha, "Effect of Hydrogen on the Stress-Rupture Strength of $2^1/_4$ Cr-1Mo Steel," *Metal Properties for the Petroleum and Chemical Industries (ASME G00103/MPC-2),* American Society of Mechanical Engineers, New York, 1976, pp. 590 – 592.

22. A. R. Ciuffreda, N. B. Heckler, and E. V. Norris, "Stress Rupture Behavior of Cr-Mo Steels in a High Pressure Hydrogen Environment," *(ASME H00227/MPC – 18),* American Society of Mechanical Engineers, New York, 1982.

23. K. R. Lewis, Shell Global Solutions—International, NACE Refin*Cor, 98C5.14

24. Exxon Research & Engineering, private communication to API Subcommittee on Corrosion and Materials, August 1995.

25. D. C. Cherrington and A. R. Ciuffreda, "Design of Piping Systems for Hydrogen Service," *Proceedings*, Division of Refining, 1967, Volume 47, American Petroleum Institute, New York, pp. 237 – 252.

26. T. Ishiguro, K. Kimura, T. Hatakeyama, T. Tahara and K. Kawano, "Effect of Metallurgical Factors on Hydrogen Attack Resistance in C-0.5Mo Steel," presented at the Second International Conference on Interaction of Steels with Hydrogen in Petroleum Industry Pressure Vessel and Pipeline Service, The Materials Properties Council, Inc., Vienna, Austria, October 19 – 21, 1994.

27. M. H. Armbruster, "The Solubility of Hydrogen at Low Pressure in Iron, Nickel, and Certain Steels at 400 to 600C," *J. Am. Chem. Soc. 65,* p 1043, 1943.

28. W. Geller and T. Sun, "Influence of Alloy Additions on Hydrogen Diffusion in Iron and Contribution to the System Iron-Hydrogen," *Arch. Eisenhuttenw 21*, pp. 423 – 430, 1950.

29. T. P. Groeneveld and A. R. Elsea, "Permeation of Hydrogen at Elevated Temperatures and Pressures Through Stainless Steel-Overlayed 2.25Cr-1Mo Steel," *Proceedings of American Petroleum Institute, Division of Refining, Vol. 56* (Midyear Meeting, May 9–12, 1977, Chicago, IL), pp. 7 – 16. API, Washington, D.C., 1977.

30. "Report on the Effect of Stainless Steel Weld Overlay or Cladding on Hydrogen Attack of Underlying Steel," Materials Properties Council, New York, September 1984.

31. Archakov and Grebeshkova, Reference 105 in *Welding Research Council Bulletin 275*, "The Use of Quenched and Tempered 2.25 Cr-1Mo Steel for Thick Wall Reactor Vessels, etc.," W. E. Erwin, J. C. Kerr, February 1982.

32. Exxon Report: "Hydrogen Attack Of Gofiner Reactor Inlet Nozzle," 1988.

33. G. R. Prescott, "History and Basis of Prediction of Hydrogen Attack of C-0.5Mo Steel," a state-of-the-art review presented at Second International Conference on Interaction of Steels with Hydrogen in Petroleum Industry Pressure Vessel and Pipeline Service, The Materials Properties Council, Inc., Vienna, Austria, October 19 – 21,1994.

34. W. D. Wang, "Inspection of Refinery Vessels for Hydrogen Attack Using Ultrasonic Techniques," Review of Progress in *Quantitative Nondestructive Evaluation*, Vol. 12, D. O. Thompson and D. E. Chement, Plenum Press, New York.

35. Weicheng D. Wang, "Ultrasonic Detection of High Temperature Hydrogen Attack," United States Patent #5,404754, Issued April 11, 1995.

36. W. David Wang, "Ultrasonic Detection, Characterization, and Quantification of Localized High Temperature Hydrogen attack in Weld Heat Affected Zone," *In Service Experience in Fossil and Nuclear Power Plants,* PVP-Vol. 392, Edited by J. Pan, ASME, New York, 1999, pp. 291 – 298.

37. Weicheng David Wang, "Ultrasonic Techniques for Inspection of Weld and Heat-Affected Zone for Localized High Temperature Hydrogen Attack," United States Patent #6,125,704, Issued Oct. 3, 2000.

38. R. Bruscato, "Temper Embrittlement and Creep Embrittlement of 2.25Cr-1Mo Shielded Metal-Arc Weld Deposits," Weld. J. 49, Res. Suppl., pp 148-s – 156-s, April 1970.

3 Operating Limits

3.1 BASIS FOR SETTING OPERATING LIMITS

Figure 1 illustrates the resistance of steels to attack by hydrogen at elevated temperatures and hydrogen pressures. As explained below, high temperature hydrogen attack of steel can result in surface decarburization, internal decarburization and fissuring, or both. 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 one 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 or ASME.

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. A major exception has been for C-0.5Mo steel. This edition consolidates all information relevant to 0.5Mo steels (C-0.5Mo and Mn-0.5Mo) in Appendix A.

The fifth edition of this recommended practice also added three data points, which show high temperature hydrogen attack of 1.25Cr-0.5Mo steel below the current 1.25Cr-0.5Mo curve. See Appendix B for more discussion of 1.25Cr-0.5Mo steel. Appendix C gives a similar discussion for 2.25Cr-1.0Mo steel.

3.2 SELECTING MATERIALS FOR NEW EQUIPMENT

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

a. Other corrosives that may be in the system, such as hydrogen sulfide.
b. Creep, temper embrittlement, or other high temperature damage mechanisms.
c. Possible synergistic effects, such as between high temperature hydrogen attack and creep.

Temperatures for data plotted in the figures represent a range in operating conditions of ±20°F (±11°C). Because Figure 1 is based largely upon empirical experience, an operating company may choose to add a safety margin, below the relevant curve, when selecting steels.

References and Comments for Figure 1

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

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, 1938, Vol. 1, No. 12, pp. 223 – 234.
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, 1933, Vol. 128, No. 2, pp. 383 – 397.
5. J. L. Cox, “What Steel to Use at High Pressures and Temperatures,” Chemical and Metallurgical Engineering, 1933, Vol. 40, pp. 405 – 409.
6. R. J. Sargant and T. H. Middleham, "Steels for Autoclaves," Chemical Engineering Congress Transactions, June 1936, Vol. I, World Power Conference, London, pp. 66 – 110.
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, 1944, Vol. 66, pp. 81 – 126.
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, 1948, Vol. 70, pp. 414 – 416.
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, 1957, Vol. 37, American Petroleum Institute, New York, pp. 116 – 128.
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, 1953, Vol. 75, pp. 525 – 533.
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, 1960, Vol. 46, No. 10, pp. 1349 – 1352.
26. K. L. Moore and D. B. Bird, “How to Reduce Hydrogen Plant Corrosion,” Hydrocarbon Processing, 1965, Vol. 44, No. 5, pp. 179 – 184.
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.

Comments

A. A section made of A 106 pipe was found to be attacked to 27% of its thickness after 5745 hours. Other pieces of pipe in the same line were unaffected.

B. The attack 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 attacked while 17 were not.

D. After 2 years exposure, five out of six pieces of carbon steel pipe were attacked. One piece of pipe was unaffected.

E. Attack was concentrated in the weld and heat-affected sections of A 106 pipe. Metal on either side of this zone was unaffected.

F. After 11 years service, attack was found in the hot bent section of A 106 pipe. Unheated straight sections were not affected.

G. After 2 years service, all parts of carbon steel pipe, including weld and heat-affected zones, were satisfactory.

H. After 4 years service, weld and heat-affected zones of A 106 pipe showed cracks.

J. After 31 years 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 service, a forging of 0.3C-1.3Cr-0.25Mo steel was unaffected.

N. After 7 years service, a forging of 0.3C-1.52Cr-0.50Mo steel showed cracks 0.050 in. (1.3 mm) deep.

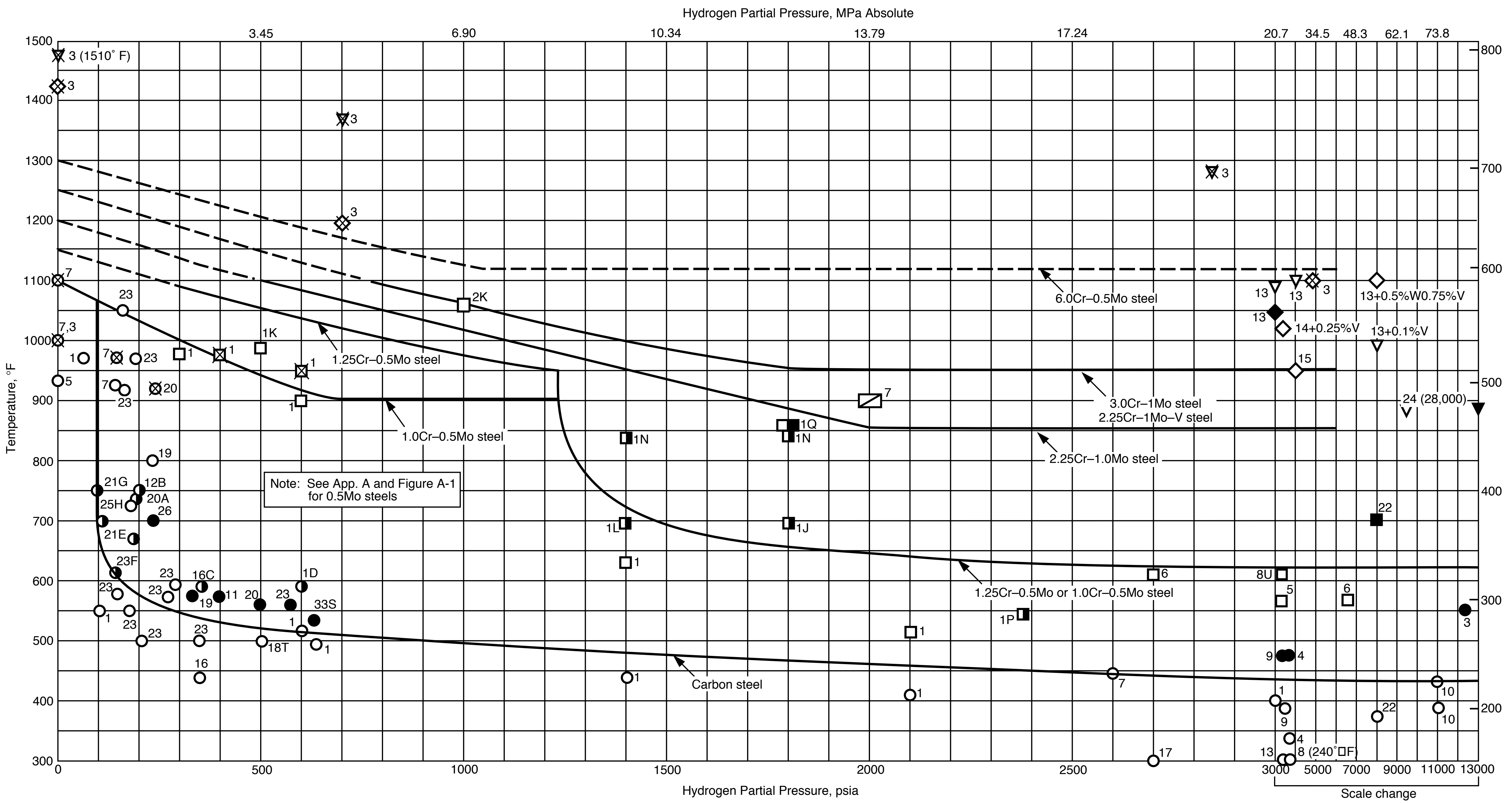
P. After 30 years service, a forging of 0.30C-0.74Cr-0.43Ni steel was unaffected.

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, 1.25Cr-0.5Mo valve body was not damaged by HTHA.



Notes:

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.
2. Austenitic stainless steels are generally not decarburized in hydrogen at any temperature or hydrogen pressure.
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 I, of the ASME code. See 5.3 and 5.4 in text for additional information.
4. Several failures of 1-1/4Cr–1Mo steel have been reported in the satisfactory region. See Appendix B for details.
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 Section 2.2.

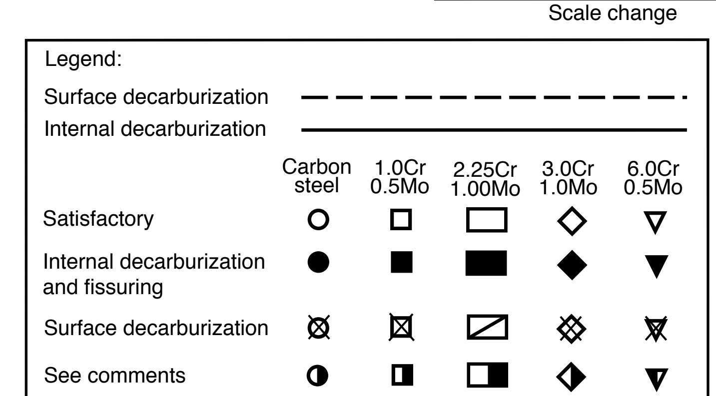


Figure 1—Operating Limits for Steels in Hydrogen Service
to Avoid Decarburization and Fissuring

4 Forms of High Temperature Hydrogen Attack

4.1 GENERAL

As noted above, high temperature hydrogen can attack steels in two ways:

a. Surface decarburization.
b. Internal decarburization and fissuring.

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 430°F (221°C), and high hydrogen partial pressure favors internal decarburization and fissuring, which can eventually lead to cracking. Both mechanisms are active at high temperatures and high hydrogen partial pressures. These mechanisms are described more fully 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 created by methane formation.

4.2 SURFACE DECARBURIZATION

Surface decarburization does not produce fissures. In this respect, it is similar to decarburization created by the 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 this 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. Carbon in solution diffuses to the surface so that the rate-controlling mechanism appears to be carbon diffusion. Inasmuch as the carbon in solution is continuously supplied from the carbides, 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. Naumann's work, which is based on 100-hour tests, indicates decarburization tendencies; however, long-time exposures have indicated lower operating limits.

4.3 INTERNAL DECARBURIZATION AND FISSURING

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 50 years. At temperatures above and to the right of the solid curves, internal decarburization and fissuring/cracking occurs. Internal decarburization and fissuring are preceded by an incubation period that depends on temperature and hydrogen partial pressure (see Section 5.2 for further discussion).

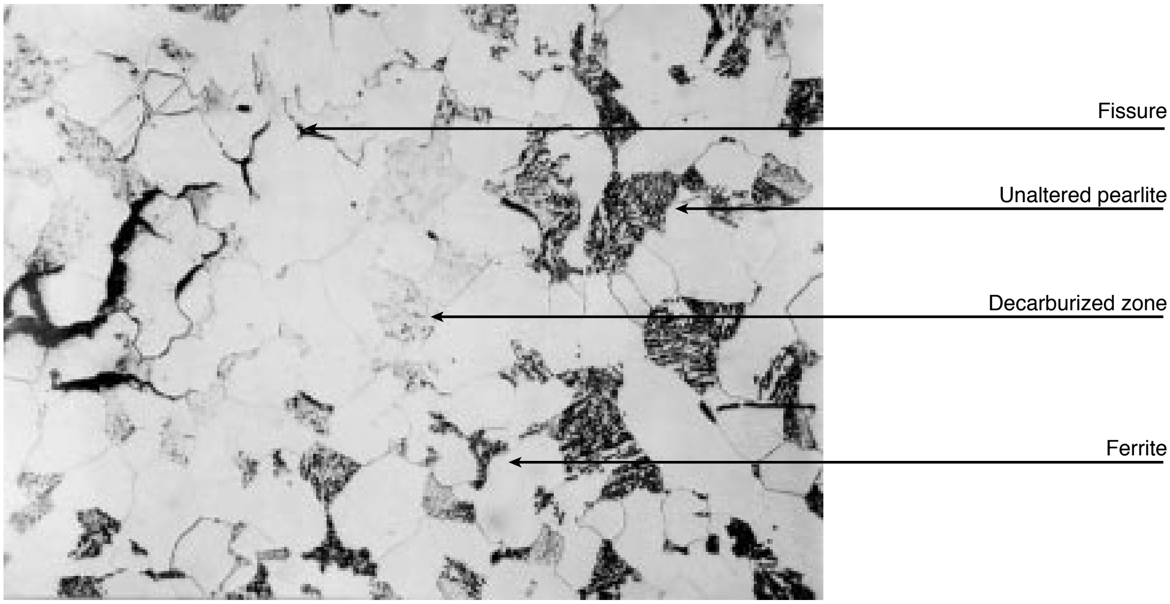
Internal decarburization and fissuring are caused by hydrogen permeating the steel and reacting with carbon to form methane.[5] The methane formed cannot diffuse out of the steel and typically accumulates at grain boundaries. This results in high localized stresses which lead to the formation of fissures, 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 reduce the number of nucleation sites by forming more stable alloy carbides which resist breakdown by hydrogen and, therefore, 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. When steel contains segregated impurities, stringer-type inclusions or laminations, hydrogen or methane accumulations in these areas may cause severe blistering.[7]

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



Notes:

1. 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.
2. Magnification: 520x; nital etched.

Figure 2—C-0.5Mo Steel (ASTM A 204-A) Showing Internal Decarburization and Fissuring in High Temperature Hydrogen Service

5 Factors Influencing HTHA

5.1 HIGH TEMPERATURE HYDROGEN ATTACK IN A LIQUID HYDROCARBON PHASE

High temperature hydrogen attack 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 in equilibrium. Recent plant experience and testing of field-exposed specimens have shown that high temperature hydrogen attack can occur under such conditions.[10]

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

5.2 INCUBATION TIME

Damage to steels by high pressure, high temperature hydrogen is preceded by a period of time when no noticeable change in properties is detectable by current mechanical testing methods. After this period of time has elapsed, material damage is evident with resultant decreases in strength, ductility, and toughness. The length of time before high temperature hydrogen attack can be detected by usual mechanical testing methods is termed the incubation period. This period varies with the type of steel and severity of exposure; it may last only a few hours under extreme conditions and become progressively longer at lower temperatures and hydrogen partial pressures. With some steels under mild conditions, no damage can be detected by mechanical testing methods 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 voids at grain boundaries.

The length of the incubation period is important because it determines the useful life of a steel at conditions under which high temperature hydrogen attack occurs. Useful theoretical models of the high temperature hydrogen attack mechanism and incubation period have been proposed.[11, 12, 13] High temperature hydrogen attack can be viewed as occurring in three stages:

a. The incubation period during which mechanical properties change very slowly and the changes are not detectable.

b. The stage of rapid mechanical property deterioration associated with rapid fissure growth.

c. The final stage where carbon in solid solution is exhausted and mechanical properties reach their final value.

During the incubation period, methane pressure builds up in submicroscopic voids. These voids grow slowly due both to 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 carbon steel are given in Figure 3.[14] These can be used as a guide in determining approximate safe operating times for steels that operate above their long-term experience curves. Appendix A includes similar curves that may be useful for some heats of C-0.5Mo steel, with the precaution that resistance of C-0.5Mo steel to high temperature hydrogen attack is particularly sensitive to heat treatment, chemical composition, and the heating/cooling history of the steel during forming.[15, 16, 17, 18]

5.3 EFFECT OF PRIMARY STRESSES

Many users have reported satisfactory performance of annealed or normalized and tempered steels produced before 1969, as shown in Figure 1. These steels have been used for pressure-retaining equipment at design stress levels allowed by the 1969 or earlier editions of commonly-accepted codes (such codes include the ASME Code, Section VIII, Division 1; the standards of the American National Standards Institute; and, for the lower-strength materials, those of Deutsche Industrie-Normen). However, pressure vessels in hydrogen service have also been constructed using the higher allowable stresses permitted in Section VIII, Division 2, or modifications of Section III of the ASME Code. Quenched and tempered or normalized and tempered steels have normally been utilized for these vessels due to their improved mechanical properties (strength and impact toughness).

No incidents of decarburization or fissuring of pressure vessels built to the specifications of Section VIII, Division 2, of the ASME Code have been reported. None of the failure data in Figure 1 represent materials used at the higher allowable stresses.

Published laboratory creep studies[19] have shown that the rupture strength and rupture ductility of 2.25Cr-1Mo steel are diminished when tested in hydrogen as compared to their values in air. These tests were a continuation of previously-reported tests[20, 21, 22] that showed somewhat conflicting results in shorter term tests.

These tests were conducted at applied stress levels similar to those that might be experienced by ASME Section VIII, Division 2 vessels. Test exposure times exceeded 50,000 hours depending on applied stress and temperature. The test specimens were from weldments of thick section plates and represented base metal, weld metal, and heat-affected zone. Detrimental effects of hydrogen were found down to the Figure 1 limit of 850°F (454°C) at 2000 psia (14 MPa) and 3000 psia (21 MPa) hydrogen partial pressure. In rare cases unusually high localized stresses have caused high temperature hydrogen attack under temperature and hydrogen partial pressure conditions that are not expected to cause damage according to the Figure 1 curves.[23] However, there is no report of HTHA below the Figure 1 limits when stresses are within ASME Code limits.

5.4 EFFECT OF SECONDARY STRESSES

High temperature hydrogen attack 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 high temperature hydrogen attack 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 work sponsored by API and summarized in API Publication 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 produced by high temperature hydrogen attack are developed.

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.

5.5 EFFECT OF HEAT TREATMENT

Both industry experience and research work indicate that postweld heat treatment (PWHT) of chromium-molybdenum steels in hydrogen service improves resistance to high temperature hydrogen attack. The PWHT stabilizes alloy carbides. This reduces the amount of carbon available to combine with hydrogen, thus improving high temperature hydrogen attack 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 high temperature hydrogen attack resistance of 2.25Cr-1Mo steel.[19] In these tests, 2.25Cr-1Mo steels postweld heat treated for 16 hours at 1275°F (691°C) showed more resistance to high temperature hydrogen attack than the same steels postweld heat treated for 24 hours at 1165°F (630°C). Both high PWHT temperatures and longer times are beneficial. Similarly, high temperature hydrogen attack 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 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 higher PWHT temperatures can affect the ability to meet ASME Code Class 2 strength requirements.

5.6 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] A sound, metallurgically bonded austenitic stainless steel cladding or weld overlay can reduce the effective hydrogen partial pressure acting on the base metal. Ferritic or martensitic claddings or weld overlays have little or no benefit in reducing the hydrogen partial pressure acting on the base metal.

The amount of hydrogen partial pressure reduction depends on the materials and the relative thickness of the cladding/weld overlay and the base metal. The thicker the austenitic stainless steel barrier is relative to the base metal, the better.[30] Archakov and Grebeshkova[31] mathematically considered how stainless steel corrosion barrier layers increase resistance of carbon and low alloy steels to high temperature hydrogen attack.

There have been a few instances of high temperature hydrogen attack 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] high temperature hydrogen attack 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 high temperature hydrogen attack of C-0.5Mo steel occurred under intergranularly cracked Type 304 austenitic stainless steel cladding (see data point 51U in Appendix A). The other cases involved ferritic or martensitic stainless steel cladding.

It is not advisable to take a credit for the presence of an austenitic stainless steel cladding/weld overlay when selecting the base metal for a new vessel or when operating an existing vessel long term in high temperature hydrogen service. Some operators have successfully taken some credit for the presence of an austenitic stainless steel cladding/weld overlay for short-term operation when conditions only marginally 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.

6 Inspection for HTHA

The selection of optimum inspection methods and frequencies for high temperature hydrogen attack in specific equipment or applications is the responsibility of the user. The information below and in Tables D-1 and D-2 are intended to assist the user in making such decisions.

Experience with steels operated below their respective Figure 1 Nelson curves has been good. Consequently, most users do not inspect equipment for high temperature hydrogen attack damage unless it has been operated near or above its curve. A high temperature attack 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 high temperature hydrogen attack occurring at conditions below the curves have been reported to the API (see Appendixes A, B, and C). Most of these have involved C-0.5Mo steel.[33] 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 HTHA 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. See Appendix A.

High temperature hydrogen attack 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.

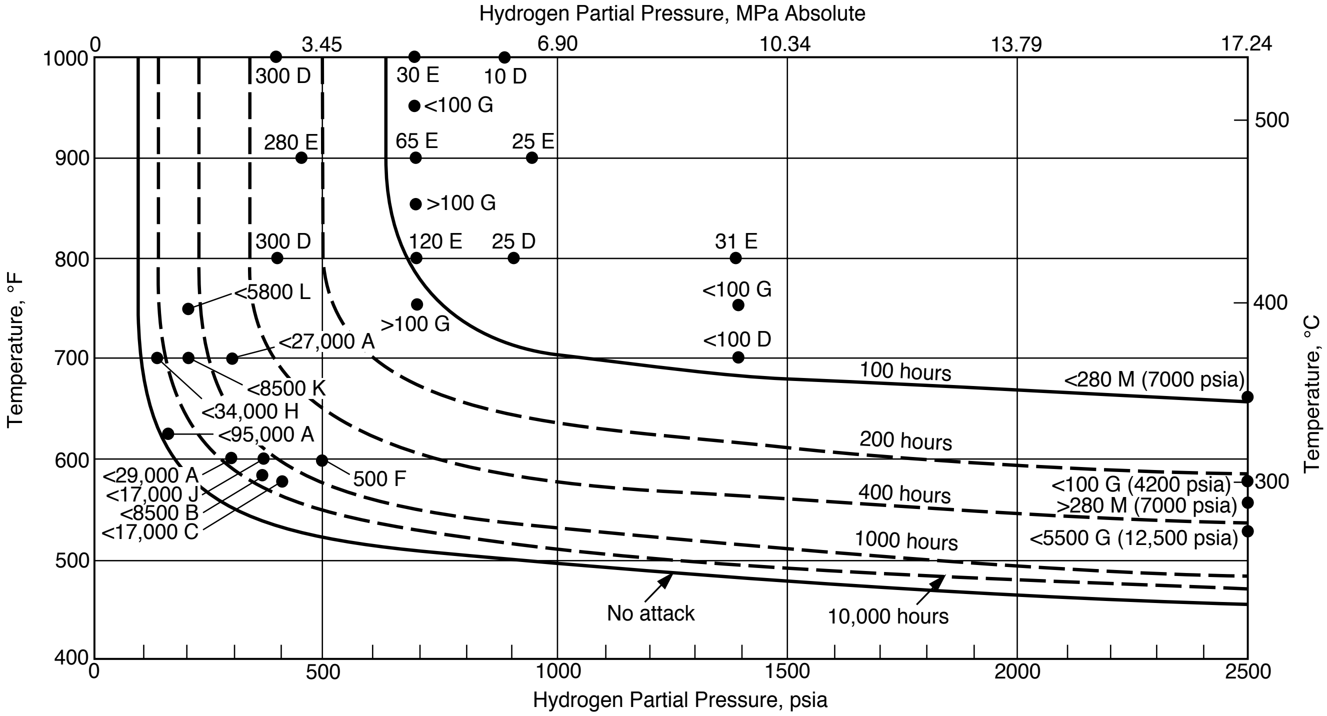
Tables D-1 and D-2 provide a summary of available methods of inspection for HTHA damage, including a discussion of the advantages and limitations of each. Two or more inspection methods are often used in combination to overcome the limitations of any single method.[34, 35]

High temperature hydrogen attack 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 general attack of the base metal, high temperature hydrogen attack has been known to occur as a very narrow band of intense attack and cracking, running alongside and parallel to welds. This highly localized form of attack requires special nondestructive testing (NDT) techniques for detection, such as high frequency shear wave and angle-beam spectrum analysis.[36, 37]

For base metal examination, ultrasonic testing (UT) methods have the best chance of detecting high temperature hydrogen attack damage in the fissuring stage. 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 high temperature hydrogen attack only after discrete cracks have formed and there is significant degradation of mechanical properties.

For weldment examination, only two UT methods of examination are considered effective. High frequency shear wave and angle-beam spectrum analysis techniques should be used to detect high temperature hydrogen attack damage in the fissuring stage. Conventional shear wave UT and time of flight diffraction (TOFD) techniques can be used 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. In situ metallography can be effective in detecting the early stages of high temperature hydrogen attack (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 D-2).



References

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

B. A. R. Ciuffreda and W. D. Rowland, "Hydrogen Attack of Steel in Reformer Service," *Proceedings, 1957,* Vol. 37, American Petroleum Institute, New York, pp. 116 – 128.

C. C. A. Zapffe, "Boiler Embrittlement," *Transactions of the ASME,* 1944, Vol. 66, pp. 81 – 126.

D. R. E. Allen, R. J. Jansen, P. C. Rosenthal, and F. H. Vitovec, "The Rate of Irreversible Hydrogen Attack of Steel at Elevated Temperatures," *Proceedings, 1961,* Vol. 41, American Petroleum Institute, New York, pp. 74 – 84.

E. L. C. Weiner, "Kinetics and Mechanism of Hydrogen Attach of Steel," Corrosion, 1961, Vol. 17, pp. 109 – 115.

F. J. J. Hur, J. K. Deichler, and G. R. Worrell, "Building a Catalytic Reformer?," *Oil and Gas Journal,* October 29, 1956, Vol. 54, No. 78, pp. 103 – 107.

G. F. K. Naumann, "Influence of Alloy Additions to Steel Upon Resistance to Hydrogen Under High Pressure," *Technische Mitteilungen Krupp,* 1938, Vol. 1, No. 12, pp. 223 – 234.

H. M. Hasegawa and S. Fujinaga, "Attack of Hydrogen on Oil Refinery Steels," *Tetsu To Hagane,* 1960, Vol. 46, No. 10, pp. 1349 – 1352.

I. T. C. Evans, "Hydrogen Attack on Carbon Steels," *Mechanical Engineering,* 1948, Vol. 70, pp. 414 – 416.

J. Air Products, Inc., private communication to API Subcommittee on Corrosion, March 1960.

K. API Refinery Corrosion Committee Survey, 1957.

L. I. Class, "Present State Knowledge in Respectto the Properties of Steels Resistant to Hydrogen Under Pressure," *Stahl and Eisen,* August 18, 1960, Vol. 80, pp. 1117 – 1135.

Notes:

1. This figure was adapted from Figure 3, Fourth Edition (1990) of this publication.

2. Numbered and lettered references for points in this figure refer to data listed in Table A-1 and Figure A-1 comments.

Figure 3—Time for Incipient Attack of Carbon Steel in High Temperature Hydrogen Service

APPENDIX A—HIGH TEMPERATURE HYDROGEN ATTACK OF 0.5Mo STEELS

A.1 General

The purpose of this appendix is to provide a brief summary of the information and experience regarding the use of 0.5Mo (C-0.5Mo, 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 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 th+*e position of the 0.5Mo curve.[A1, A2] 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 high temperature hydrogen attack 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 high temperature hydrogen attack of C-0.5Mo steel equipment as much as 200°F (111°C) below the curve. Plant experience has identified 27 instances of high temperature hydrogen attack 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 have been reported of high temperature hydrogen attack of Mn-0.5Mo steel 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 high temperature hydrogen attack. Many heats seem to have resistance at conditions indicated by the 0.5Mo curve on Figure A-1. However, some heats seem to have high temperature hydrogen attack resistance only marginally better than carbon steel. Work [A2, A3, A4, A5] relating its resistance to high temperature hydrogen attack to the thermal history of the steel give some guidance as to why. Slow-cooled, annealed C-0.5Mo steels have less resistance to high temperature hydrogen attack than normalized steels. The studies have shown that postweld heat treatment improves the high temperature hydrogen attack resistance of weldments and heat affected zones 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 high temperature hydrogen attack resistance after postweld heat treatment. The initial studies suggest that this is due to free carbon being present in the ferrite matrix after postweld heat treatment. Normalized C-0.5Mo steel base metals, on the other hand, show improvement in high temperature hydrogen attack resistance following tempering or postweld heat treatment. Such normalized and postweld heat treated 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 high temperature hydrogen attack resistance of C-0.5Mo are better understood, each user should carefully assess the use of C-0.5Mo steel in services above the carbon steel curve in Figure A-1.

Existing C-0.5Mo steel equipment that is operated above the carbon steel curve in Figure A-1 should be inspected to detect high temperature hydrogen attack. Owner/operators should evaluate and prioritize C-0.5Mo equipment operating above the carbon steel limit for inspection, as addressed by Hattori and Aikawa.[A6] 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: (1) Figure A-2 which shows the effect of trace alloying elements (molybdenum) on operating limits, and (2) Figure A-3 which shows 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 high temperature hydrogen attack resistance of steels. The data in Figures A-2 and A-3 should be used with caution, since some heats of C-0.5Mo steels have suffered high temperature hydrogen attack 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 high temperature hydrogen attack listed in Table A-1 and plotted on Figure A-1 are also shown for reference in Figure A-3. The incubation time would be less than the service life at the time the attack was detected.

A.2 References

A1. R. D. Merrick and A. R. Ciuffreda, "Hydrogen Attack of Carbon-0.5-Molybdenum Steels," 1982 Proceedings, Refining Department, Volume 61, American Petroleum Institute, Washington, D.C., pp. 101 – 114.

A2. M. C. Maggard, "Detecting Internal Hydrogen Attack," *Oil and Gas Journal,* March 10, 1980, pp. 90 – 94.

A3. K. Ishii, K. Maeda, R. Chiba, and K. Ohnishi, "Intergranular Cracking of C-0.5Mo Steel in a Hydrogen Environment at Elevated Temperatures and Pressures," 1984 Proceedings, Refining Department, Volume 63, American Petroleum Institute, Washington, D.C., pp. 55 – 64.

A4. R. Chiba, K. Ohnishi, K. Ishii, and K. Maeda, "Effect of Heat Treatment on the Resistance of C-0.5Mo Steel Base Metal and Its Welds to Hydrogen Attack," 1985 Proceeding, Refining Department, Volume 64, American Petroleum Institute, Washington, D.C., pp. 57 – 74.

A5. T. Ishiguro, K. Kimura, T. Hatakeyama, T. Tahara and K. Kawano, "Effect Metallurgical Factors on Hydrogen Attack Resistance in C-0.5Mo," presented at the Second International Conference on Interaction with Hydrogen in Petroleum Industry Pressure Vessel and Pipeline Service, The Materials Properties Council, Inc., Vienna, Austria, October 19 – 21,1994.

A6. Hattori, K. and Aikawa, S., "Scheduling and Planning Inspection of C-0.5Mo Equipment Using The New Hydrogen Attack Tendency Chart," pvp.Vol. 239/MPC-Vol. 33, Serviceability of Petroleum Process and Power Equipment, ASME, 1992.

References and Comments for Figure A-1

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

References

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

7. Standard Oil Company of California, private communication to API Subcommittee on Corrosion.

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

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.

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. [M]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 (10).

46. [K,E]JGC Corporation/Japan Steel Works, Exxon Corporation.

47. [L]JGC Corporation/Japan Steel Works, API Midyear Refining Meeting, 1985.

48. [M]Air Products & Chemicals, Inc., private communication to API Subcommittee on Corrosion and Materials Engineering, 1985.

49. [S]Texaco USA, API Fall Refining Meeting, 1985.

50. [T]Mobil R&D Corporation, private communication to API Subcommittee on Corrosion and Materials Engineering, 1986.

51. [U]Shell Oil Company, private communication to API Subcommittee on Materials Engineering and Inspection, 1987.

52. [V]Texaco, Inc., private communication to API Subcommittee on Corrosion, 1981.

53. Kemira, B. V., private communication to API subcommittee on Materials Engineerings & Inspection, 1986.

54. [AA]Chevron Research and Technology Company, private communication to API Subcommittee on Corrosion and Materials, June 1992.

55. [BB]Chevron Research and Technology Company, private communication to API Subcommittee on Corrosion and Materials, June 1992.

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.

Comments

A. Feed line pipe leaked; isolated areas damaged.Blistered, decarburized, fissured; postweld heat treated at 1100°F to 1350°F.

B. Effluent line, pipe and heat-affected zone, isolated areas damaged; no postweld heat treatment.

C. Weld and pipe, isolated areas damaged; no postweld heat treatment.

D. Effluent line; weld, isolated areas damaged; postweld heat treatment.

E. Feed line; weld and heat-affected zone, isolated areas damaged; postweld heat treatment.

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

G. Effluent exchanger channel; welds, plate, and heat-affected zone, isolated areas damaged; postweld heat treatment.

H. Effluent exchanger channel; welds, plate, and heat-affected zone, isolated areas damaged; postweld heat treated at 1100°F.

I. Catalytic reformer, combined feed/effluent exchanger shell; plate; postweld heat treated at 1250°F.

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

K. Catalytic reformer combined feed piping; welds and base metal; postweld heat treatment.

L. Gas-oil hydrodesulfurization unit.Elbow cracked intergranularly and decarburized at fusion line between weld metal and heat-affected zone; no postweld heat treatment.

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; postweld heat treated 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; postweld heat treated 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.

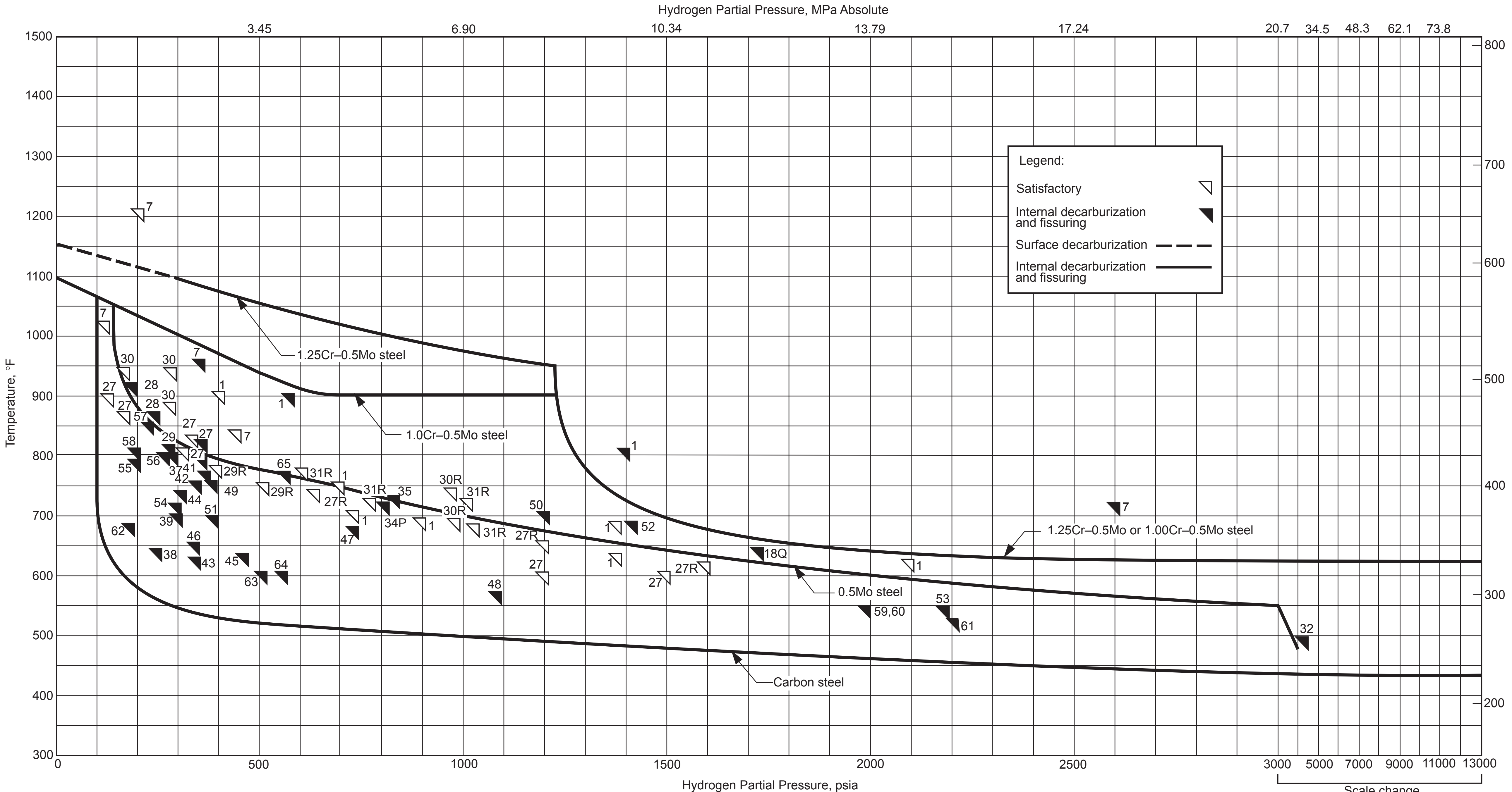
II. Blistering and base metal attack in a heat exchanger shell.

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.



Notes:
1. References and comments are shown on Table A-1
2. Curves for carbon steel, 1.0Cr–0.5Mo steel, and 1.25Cr–0.5Mo steel are included for reference.
3. The symbol { is retained as a reference against previous revisions of this publication.
4. Reference numbers are the same as in previous editions of this publication.
5. The 0.5Mo steel curve is the same as the one shown in the fourth edition of this publication (1990).

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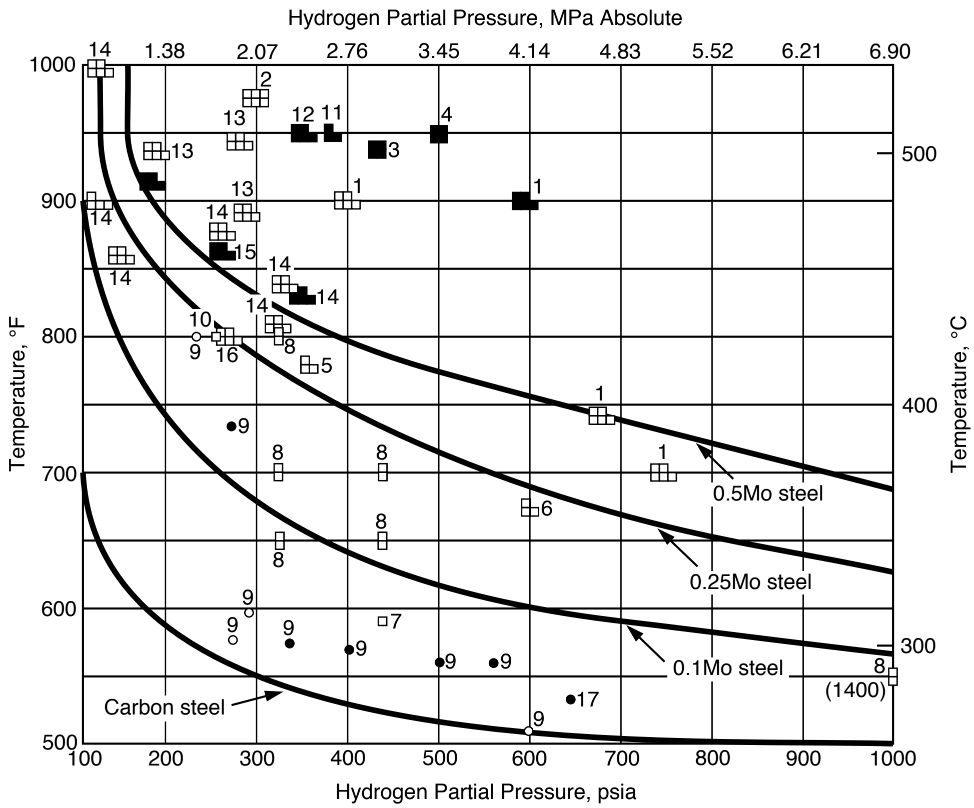
Figure A-1—Experience with C–0.5Mo and Mn–0.5Mo Steel in High Temperature Hydrogen Service

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

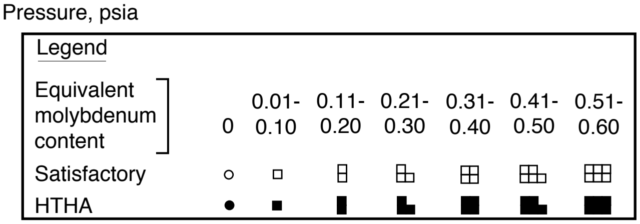
	Temperature		Hydrogen Partial Pressure (Absolute)		Service Hours	Degrees Below 0.5Mo Curve (Approximate)	
Point	°F	°C	psi	MPa	(Approx.)	°F	°C
36A[1]	790	421	350	2.41	80,000	20	11
37B[1]	800	427	285	1.97	57,000	30	17
38C[1]	640	338	270	1.86	83,000	180	100
39D[1]	700	371	300	2.07	96,000	125	69
41F[1]	760	404	375	2.59	85,000	40	22
42G[1]	750	399	350	2.41	150,000	60	33
43H[1]	625	329	350	2.41	150,000	185	103
44I[1]	730[2]	388[2]	313	2.16	116,000	90	50
45J[3]	620/640	327/338	457	3.15	70,000	167/147	93/82
46K[1]	626/680	330/360	350	2.41	131,000	184/130	102/72
47L[3]	684[2]	362	738	5.09	61,000	54	30
48M[5]	550/570	288/299	1060/1100	7.31/7.59	79,000	125/105	69/58
*	655/670	346/354	-	-	17,500	20/5	11/3
49S[3]	750/770	399/410	390	2.69	67,000	50/30	28/17
*	650	343	-	-	163,000	150	83
51U[3]	690	366	397	2.74	-	100	56
53W[5]	545	285	2190	15.1	140,000	45	25
54AA[1]	725/760	385/404	300/380	2.07/2.62	105,000	40/100	22/56
55BB[1]	800/850	427/454	175/190	1.21/1.31	124,000	80/30	44/17
56CC[1]	810/825	432/441	275/300	1.90/2.07	223,000	15/0	8/0
57DD[1]	850[4]	454[4]	225[4]	1.55[4]	158,000	10	6
58EE[1]	810/855	432/457	170	1.17	138,000	70/25	39/14
59FF[3]	550/600	288/316	2000	13.79	210,000	50/0	28/0
60GG[3]	550/600	288/316	2000	13.79	210,000	50/0	28/0
61HH[3]	530/600	277/316	2200	15.17	210,000	60/0	33/0
62II[3]	670/700	354/371	190	1.31	192,000	180/150	100/83
63JJ[3]	600/750	316/399	500	3.45	235,000	180/30	100/17
64KK[3]	600/770	316/410	525	3.62	283,000	170/0	94/0
65LL[3]	775	413	550	3.79	-	0	0

Notes:
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.
[1]Catalytic reformer service.
[2]Average.
[3]Hydrodesulfurizer service.
[4]Maximum.
[5]Ammonia plant.
*API task group currently resolving these points.



Notes:

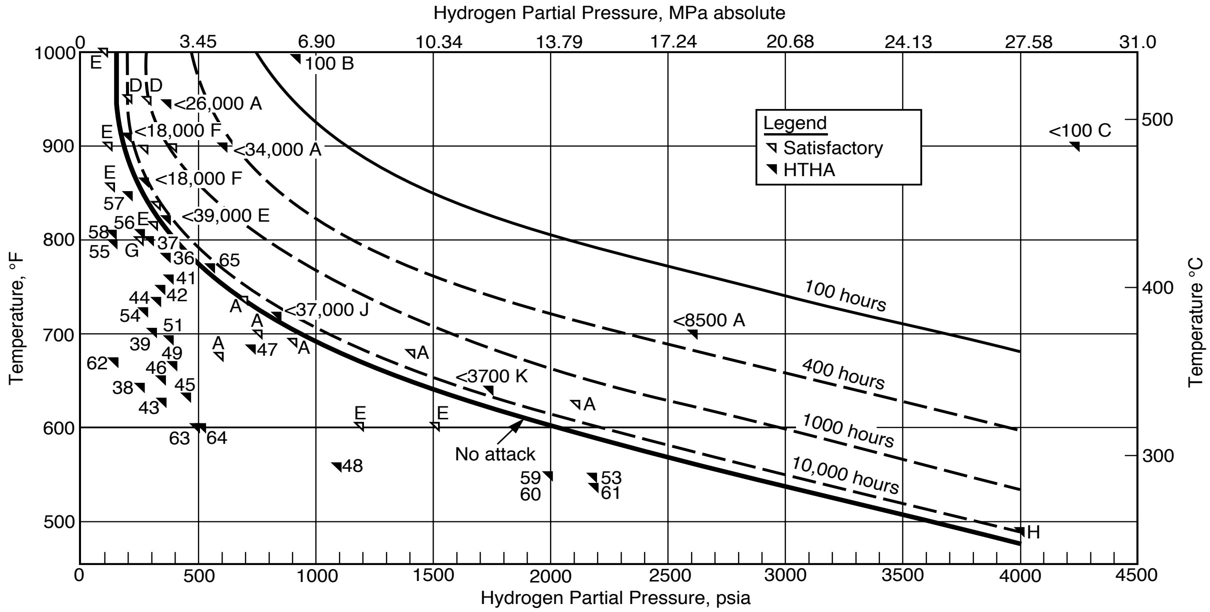
1. Mo has four times the resistance of Cr to HTHA.
2. Mo is equivalent to V, Ti, or Nb up to 0.1 percent.
3. Si, Ni, and Cu do not increase resistance.
4. P and S decrease resistance.



References	Cr	Analysis Mo	V	Mo Equiv.
1. Shell Oil Company.*		0.50		0.50
2. Weld Deposits, D. J. Bergman.*	0.79	0.39		0.59
3. Weld Deposits, D. J. Bergman.*	0.80	0.15		0.35
4. Weld Deposits, D. J. Bergman.*	0.50	0.25		0.37
5. Continental Oil Company.*		0.25		0.25
6. Standard Oil Co. of California.*		0.27		0.27
7. Standard Oil Co. of California.*	0.05	0.06	0.08	
8. A. O. Smith Corp.*			0.13 – 0.18	0.11
9. Shell Development Co., Drawing No. VT 659-2.				
10. Amoco Oil Company.*	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.*	0.11	0.43		0.50
13. Exxon Corporation.*				
14. Union Oil of California.*				
15. Amoco Oil Company.*				
16. Standard Oil Co. of California. *				
17. Gulf Oil Corporation.*				

* Private communication to the API Subcommittee on Corrosion (now Subcommittee on Corrosion and Materials).

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



Notes:
1. This figure was adapted from Figure 3, Fourth Edition (1990) of this publication.
2. Numbered and lettered references for points in this figure refer to data listed in Table A-1 and Figure A-1 comments.

Figure A-3—Time For Incipient Attack of 0.5Mo Steels in High Temperature Hydrogen Service

APPENDIX B—HIGH TEMPERATURE HYDROGEN ATTACK OF 1.25 CR-0.5MO STEEL

The purpose of this appendix is to provide a brief summary of the information and experience regarding three case histories with high temperature hydrogen attack of 1.25Cr-0.5Mo steel.

The three recent experiences with high temperature hydrogen attack are listed in Table B-1, and the operating conditions are plotted in Figure B-1.

Cases A and B were reported by Chiyoda Corporation in Japan. Case C was originally reported by Merrick and Maguire of Exxon (see Reference 7 in 2.2). 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 $\bar{x}$ equal to 31.5, as defined by Bruscato. [38]

Table B-1—Experience with High Temperature Hydrogen Attack of 1.25Cr-0.5Mo Steel at Operating Conditions below the Figure 1 Curve

	Temperature		Hydrogen Partial Pressure (Absolute)		Service Years	
Case	°F	°C	psi	MPa	°F	Description
A	960	516	331	2.28	26	1.5 NPS Schedule 80 nozzle was broken off a catalytic reformer outlet line during a shut down. 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 non-metallic 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%.
	Note 1	Note 1	Note 1	Note 1		

Note 1: Average conditions are reported as the left number. Maximum condition reported as the right number.

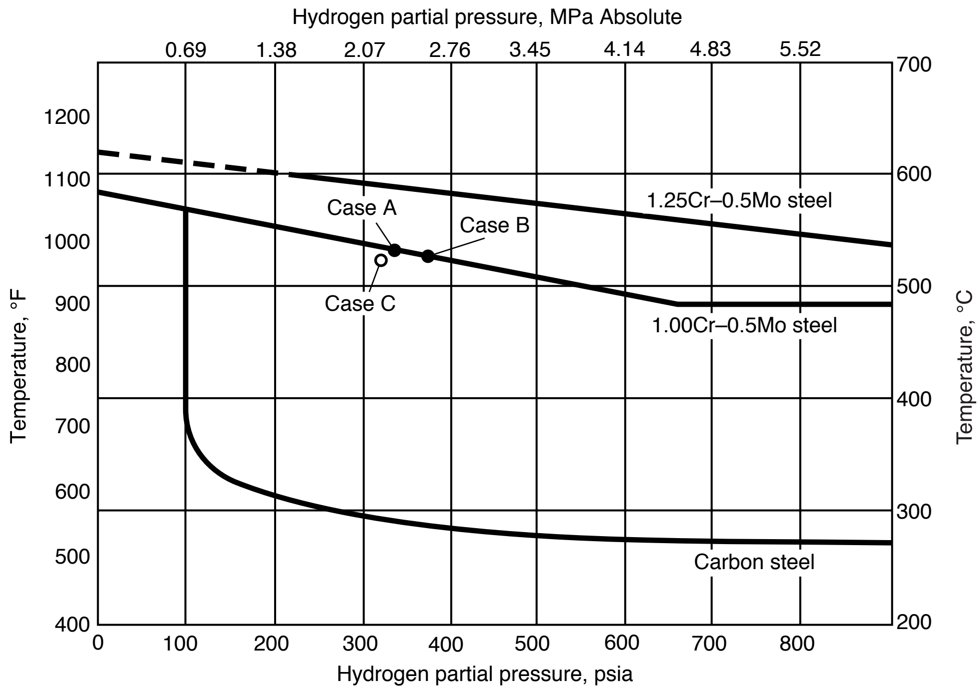


Figure B-1—Operating Conditions for 1.25Cr-0.5Mo Steels That Experienced HTHA below the Figure 1 Curve

APPENDIX C—HIGH TEMPERATURE HYDROGEN ATTACK OF 2.25CR-1MO STEEL

The purpose of this appendix is to provide a brief summary of experience regarding a case history[a] with high temperature hydrogen attack of 2.25Cr-1Mo steel.

A recent experience with high temperature hydrogen attack is described in Table C-1, and the operating conditions are plotted in Figure C-1.

This case history may indicate that highly stressed components can suffer high temperature hydrogen attack at conditions below the curve in Figure 1. In this case history, the mixing tee was believed to be highly stressed by thermal stresses due to the mixing of hot and cooler hydrogen. Figure C-1 shows 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	
°F	°C	psi	MPa	Years	Description
675/820	357/438	1385/1570	9.54/10.82	>20	A mixing tee for the hot and cold make-up 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	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.

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

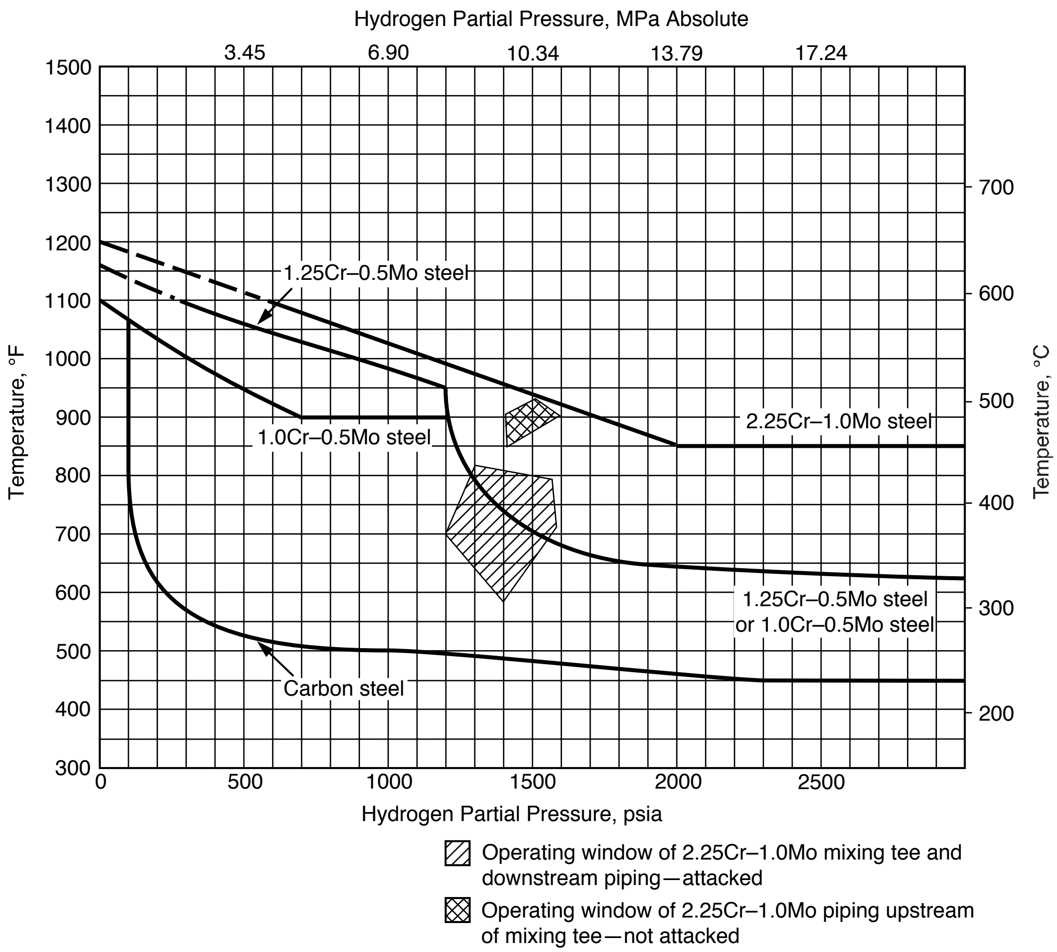


Figure C-1—Operating Conditions of 2.25Cr-1Mo Steels That Experienced HTHA below the Figure 1 Curve

APPENDIX D

Table D-1—Summary of Inspection Methods for High Temperature Hydrogen Attack

	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
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.

Table D-1—Summary of Inspection Methods for High Temperature Hydrogen Attack (Continued)

	Ultrasonic Methods										
				Backscatter					Conventional Shear Wave UT and TOFD	High Frequency Shear Wave	Angle-beam Spectrum Analysis
	Velocity Ratio	Attenuation	Spectral Analysis	Amplitude Based	Pattern Recognition	Spatial Averaging	Directional Dependence	Frequency Dependence			
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 D-1—Summary of 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 D-2—Summary of 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 to 1/8 inch (2 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 & MT techniques.	Additional development work and field trials recommended. Not currently recommended as a primary method for HTHA detection.

APPENDIX E—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 high temperature hydrogen attack (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 data sheet 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
Standards Department
1220 L Street, N.W.
Washington, D.C. 20005
standards@api.org

Data Sheet for Reporting High Temperature Hydrogen Attack 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: Port weld heat treatment Yes ______ No ______ Temperature/Time ________________ °F/hrs.

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

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

   Other ____

4. Physical 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 Hydrogen purity ________________%

7. Calculated operating stress: ________________ psia

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 Bllisters 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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	C94503	*RP 945; Avoiding Environmental Cracking in Amine Units*		82.00	
	C51008	*API 510; Pressure Vessel Inspection Code: Maintenance Inspection, Rating Repair, and Alteration*		107.00	
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