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.

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1 Scope

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

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

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

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

2 Normative References

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

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

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

API Recommended Practice 584, *Integrity Operating Windows*

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

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

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

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

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

1 ASME International, 2 Park Avenue, New York, New York 10016-5990, www.asme.org.
2 American National Standards Institute, 25 West 43rd Street, 4th Floor, New York, New York 10036, www.ansi.org.
3 American Welding Society, 8669 NW 36 Street, # 130, Miami, Florida 33166-6672, www.aws.org
4 Welding Research Council, P.O. Box 201547, Shaker Heights, Ohio 44122, www.forengineers.org