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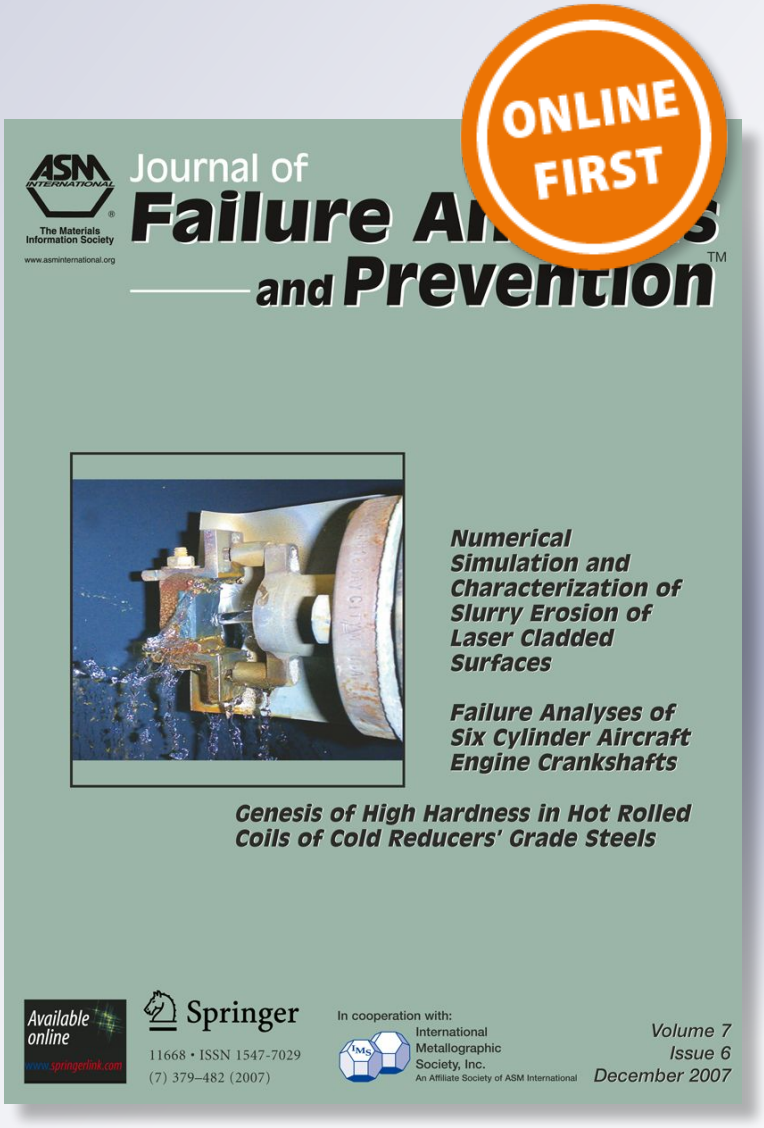

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LESSONS LEARNED

Reducing the Risk of High Temperature Hydrogen Attack (HTHA) Failures

Daniel J. Benac · Paul McAndrew

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Abstract The objective of this article is to provide lessons learned from materials, structure, and equipment failures so that costly failures can be prevented through good design, maintenance, and inspection practices, thus increasing safety, equipment reliability, and integrity of designs.

Keywords Hydrogen damage · High temperature · Failure mechanism · Ferrous metals · HTHA

Introduction

Has equipment been deteriorated by elevated temperature exposure and hydrogen? This question is frequently asked by those in ammonia, refinery, and chemical plants, who use piping, heat exchangers, and pressure vessels containing hydrogen at elevated temperatures. Beginning with research performed in the 1940s [1], equipment exposed to hydrogen at elevated temperatures is known to potentially degrade over time in a phenomenon called high-temperature hydrogen attack (HTHA). Failures of hydrogen-containing equipment can result in fires, fatal accidents, loss of production, and leaking of hydrocarbon products that can ignite, resulting in an explosion. This article discusses some of the necessary safety considerations and controls used by plant designers and operators to reduce the risk of failure of such equipment.

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HTHA Phenomenon

High-temperature exposure of the carbon and low-alloy steels used for piping and pressure vessels (Fig. 1) used in high-pressure hydrogen service leads to a special form of degradation known as HTHA, sometimes called hydrogen attack. Note that this is not the same as hydrogen embrittlement which degrades toughness at low temperatures. HTHA leads to degradation of material properties at elevated operating temperatures, but like hydrogen embrittlement, HTHA can result in sudden and catastrophic brittle failure.

Some equipment involves the use of, or production of, hydrogen at pressures greater than 0.8 MPa (100 psig) and at temperatures of 230 °C (450 °F) or above. These service conditions can lead to deterioration of carbon steel components and result in equipment failure, notably of pressure vessels and piping.

Under the influence of certain temperature conditions and hydrogen partial pressure, atomic hydrogen permeates the steel and reduces iron carbide (Fe_3C) in the steel to form methane (CH_4). Note that the methane does not diffuse from the metal, and its pressure may exceed the cohesive strength of the metal, causing fissuring between grains (Fig. 2). When fissuring occurs, the ductility of the metal is significantly and permanently lowered. The severity of hydrogen attack increases with increasing temperature and hydrogen partial pressure.

Usually, hydrogen attack occurs in three stages:

1. Atomic hydrogen diffuses into the metal,
2. Decarburization occurs (in steel), and
3. Intergranular fissuring occurs [2].

A metal in the first stage of hydrogen attack suffers only a temporary loss in ductility, since the ductility of the metal

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Fig. 1 Pressure vessels, heat exchangers, and piping equipment, which are often exposed to high-temperature hydrogen attack (HTHA) conditions

can be restored by heating. During stage two of decarburization, an attack can be confined to the surface in a surface attack, or it can occur internally, where the resultant product—methane—is unable to escape, leading to permanent internal damage. Methane bubbles nucleate as the carbides grow under methane pressure and can then link up to form fissures, cracks, and/or blisters.

If the internal pressure generated by entrapped methane exceeds the strength of the metal and fissuring occurs, then the result is permanent, irreversible embrittlement. Consequently, permanent embrittlement occurs during the second and third stages of a HTHA.

HTHA Industry Standard

The operating limits for steels can be empirically described using the operating temperature and the hydrogen partial pressure, as originally discussed by Nelson in 1949 and in API recommended practice 941, "Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants."

Since the 1970s, empirical data have been collected from operating plants and tests to establish operating limits of carbon steel and low alloy steel equipment in hydrogen service at elevated temperatures. API 941 provides guidance on those limits.

Using API 941, if a piece of equipment or piping is operated above the API 941 (Nelson) curve, then the material is not suitable for service under those conditions.

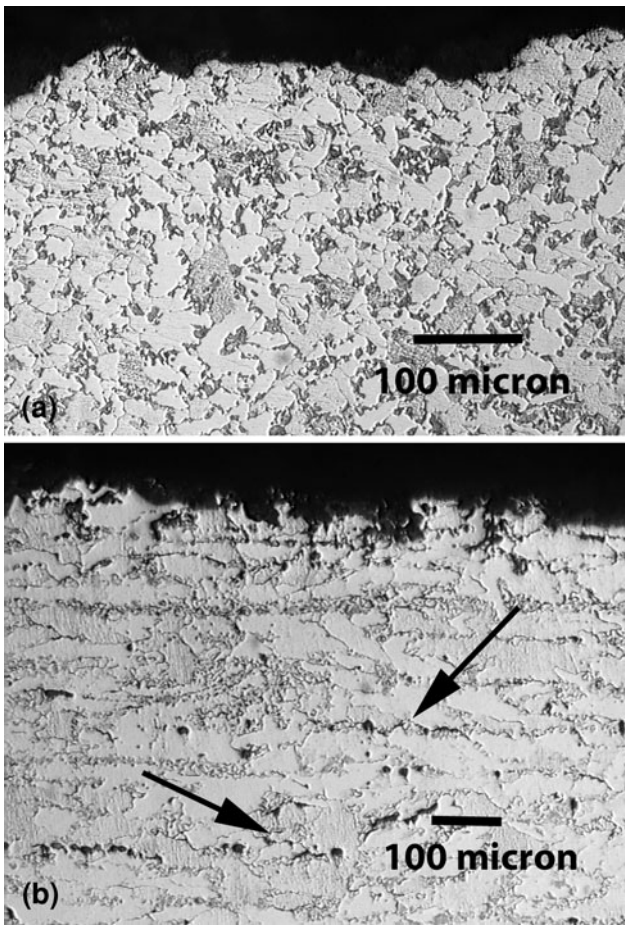

Fig. 2 (**a**) Undamaged carbon steel refinery line. (**b**) Hydrogen-damaged carbon steel refinery line. Decarburization and fissuring region caused by hydrogen depleting the iron carbides. Nital etch

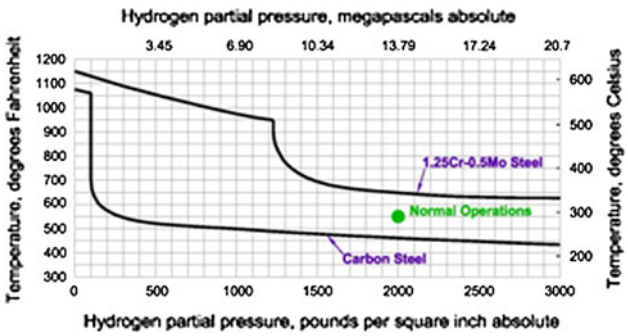

Fig. 3 Illustration of API 941 (Nelson) curve—material selection for equipment exposed to hydrogen at elevated temperature and pressures should follow API 941 guidelines

For example, if the normal operating conditions are a temperature of 288 °C (550 °F) and 13.79 MPa (2,000 psig) hydrogen partial pressure, as illustrated in Fig. 3, then the carbon steel in this case is not suitable for service under those conditions. There would be a high risk of premature failure in a relatively short time of exposure. Either the temperature or the pressure would have to drop below the

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carbon steel curve, or chromium alloyed steel should be considered for use instead. The selection of a 1¼ Cr–½ Mo material would be the preferred choice.

Using API 941, the following practices should be considered:

1. Selecting the proper material for the operating conditions, and for increased temperatures, considering the use of alloys with higher weight percents of chromium and molybdenum.
2. Using actual operating temperatures for assessing HTHA susceptibility and validating that the actual operating temperatures and pressures are below API 941 curve by a defined amount.
3. Employing experienced individuals who understand the HTHA phenomenon as well as the API 941 recommended practices.

Operating Conditions

To perform an adequate assessment of HTHA susceptibility, the operating conditions of the equipment must be known. Typical or possible design limits are not sufficient. A good HTHA assessment requires validation of data with process engineering involvement and actual field data. The key parameter is that the actual conditions to which the metal wall has been exposed must be known.

In determining the actual conditions, the placements of temperature and pressure indicators are important, as well as knowing whether excursions and process creep conditions have occurred over a period of time. Once the HTHA limits are determined, safe operating limits with necessary process alarms should be established, and a response plan should be implemented for safe operations when those limits are exceeded. Plant operations should consider the following practices:

1. Performing regular process hazard assessment of the operating conditions including changes in pressure, temperatures or partial pressure of hydrogen.
2. Verifying the actual operating conditions that the equipment experiences through good field data.
3. Installing pressure and temperature indicators at locations that measure the actual operating conditions of equipment that could be susceptible to HTHA.
4. Determining whether process creep that may affect the metal has occurred.
5. Evaluating material or operating changes using a management of change (MOC) process.
6. Evaluating whether temperature excursions and regeneration operations have an effect on HTHA susceptibility.
7. Providing definite safe operating limits with necessary process alarms and a response plan when those limits are exceeded.

Lined Equipment

For corrosion purposes, sometimes vessels are clad, lined, or weld overlaid to protect the vessel surface. This can provide initial protection, provided hydrogen does not diffuse through the liner or migrate behind the lining or cladding. If that occurs, then the vessel wall may be susceptible to HTHA.

Refractory lining is often used to insulate a pipe or vessel to lower the metal wall temperature and is an effective way to reduce the effects of HTHA. However, the refractory can degrade, crack, or deteriorate due to operating conditions or even flexure of the refractory, allowing hot spots to form, which would elevate the metal wall temperature and possibly result in exceeding the HTHA operating limits of the equipment. Figure 4 illustrates how a degraded refractory and hot spot could result in exceeding the operating temperature limit for a carbon steel line.

One way to monitor the condition of the refractory is to perform regular infrared imaging of the equipment. (An example is illustrated in Fig. 5.)

For clad, lined, or overlaid equipment the following practices should be considered:

1. Ensuring that proper foundation support for refractory-lined equipment is in place to reduce flexure of the refractory.
2. Performing regular infrared inspections, especially on refractory-lined equipment.
3. Ensuring that the operating limit is understood, and appropriate actions are taken if the limit is exceeded.

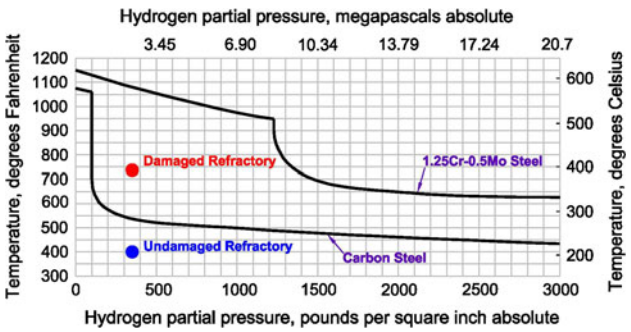

Fig. 4 Illustration of API 941 (Nelson) curve—damaged refractory can result in an increase in the metal wall temperature which if above the recommended limits could result in HTHA failure

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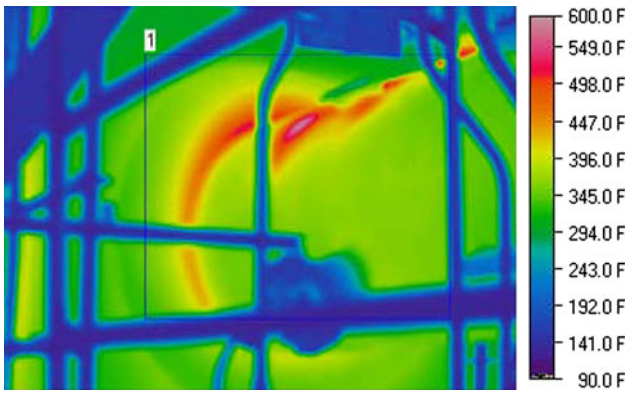

Fig. 5 Infrared image of a hydrogen-containing line showing a hot spot (red colors), due to degraded refractory

HTHA Inspection Practices

HTHA inspection requires special inspection techniques. Inspection methods used for corrosion and wall thinning are not adequate to detect HTHA, primarily because HTHA is not readily evident on the surface, as it is a subsurface phenomenon. The optimum method(s) and frequency of inspection for HTHA should be specified for specific equipment.

Accepted HTHA inspection practices include the following:

Advanced Ultrasonic Backscatter Techniques (AUBT): Ultrasonic waves backscattered from within the metal are used to evaluate subsurface microstructural features and the depth of region affected.

Phased Array: Phased Array is an ultrasonic technique based on generating and receiving ultrasounds. Instead of a single transducer and beam, phased arrays use multiple ultrasonic elements and electronic time delays to create beams by constructive and destructive interferences.

In situ metallography: This method evaluates selected surfaces by polishing, etching, and replicating of the microstructure and is limited to small locations and addresses only the surface of the material.

Positive material identification: Users of equipment are performing positive material identification (PMI) during installation of new equipment, maintenance operations, or even retro-PMI to ensure that something had not been altered previously. During installation of new equipment, welding of equipment, and maintenance operations, it is possible that the wrong material or welding rod may be used. This is not a common occurrence, but it happens. Sometimes, visual examination is performed, but often x-ray inspection is needed. PMI has also identified incorrect materials in hydrogen service.

The following inspection practices should be considered:

1. Selecting inspection methods and establish inspection frequencies that will detect the initial stages of HTHA.
2. Ensuring that written procedures are in place and implemented to provide guidance on inspection guidelines and intervals.
3. Possessing knowledge of the history of the equipment, and if unknown, making sure that necessary HTHA inspections are performed.
4. Considering performing PMI on a regular interval, especially during installation of new equipment, welding of equipment, and during maintenance operations.
5. Documenting all findings in an inspection program and implementing follow-up measures to ensure that findings are appropriately acted upon.

Summary

Failure of hydrogen-containing equipment can be prevented through good material selection, process controls, and regular inspection of equipment. Because HTHA is now better understood and inspections methods are more reliable, HTHA failures are being avoided. To avoid conditions that could cause HTHA, it is important that actual operating conditions are known and monitored, and regular HTHA inspections performed. When proper safety considerations and controls are established, the risk of HTHA failures is greatly reduced in ammonia, refinery, and chemical plants using tubes, heat exchangers, and pressure vessels containing hydrogen at elevated temperatures.

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