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Safety Snippet: High Temperature Hydrogen Attack (HTHA)

Introduction

High Temperature Hydrogen Attack (HTHA) is a particular concern for processes using high temperature hydrogen, such as hydrotreating and hydrocracking in oil and gas refineries. It occurs as a result of reactions between atomic hydrogen and solutes, particles or inclusions in steel. This can be the result of surface decarburization or internal decarburization and fissuring. HTHA commonly presents as the formation of methane by hydrogen and carbon present in the material. Overtime, this leads to the dissolution of carbides. As methane forms, it can be trapped within the steel, unable to diffuse out. Methane bubbles then build up within the steel, creating very high pressures which cause cavities to form in the metal. These cavities expand and link together as more methane becomes entrained in the steel, eventually leading to fissures and cracking.

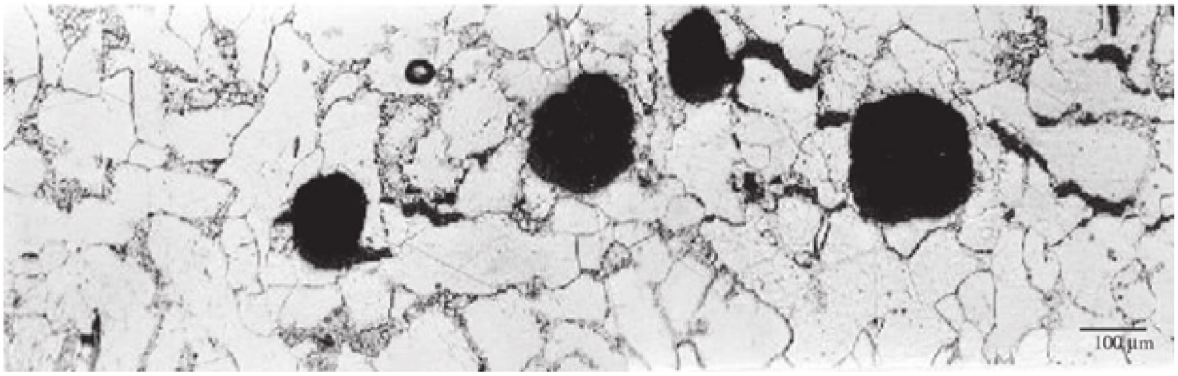


Figure 1: Voids Formed in Carbon Steel Exposed to High Temperature Hydrogen

Considerations for Minimizing HTHA Risks

- API RP 571 lists 300 Series Stainless Steel along with 5Cr, 9Cr and 12Cr alloys as being unsusceptible to HTHA when operated under normal refinery conditions.
- Processes operated under the Nelson Curve of the associated steel are less* susceptible to HTHA.
- Alloys that contain strong carbide forming elements such as zirconium, chromium, tungsten, etc. are more resistant to HTHA.
- Metals with high concentrations of less stable carbides, such as carbon steel and C-0.5Mo Steel are highly susceptible to HTHA.
- Ensure all welding is properly heat treated to limit void space that could allow for methane collection.
- Research has shown that aluminum-killed steel has a higher resistance to HTHA than steel produced using other processes.
- Fouling and other contamination in piping and equipment can increase the rate at which HTHA takes place.

*The US Chemical Safety Board has stressed that operating under the Nelson Curve is NOT sufficient as the only measure to prevent HTHA related damage.

In This Issue

Hazards and considerations associated with High Temperature Hydrogen Attack (HTHA) are discussed, along with testing mechanisms, relevant standards, a Case Study, and a CSB Safety Alert.

Safety Snippets are published monthly and can be located on the Nebula Safety & Environmental LinkedIn page or website.

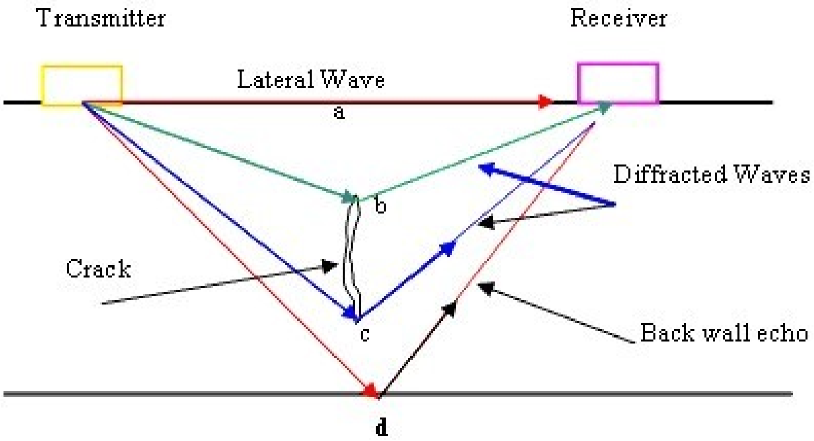
https://www.NebulaSafety.com

Testing

It is difficult to detect HTHA using non-destructive methods before it has caused hazardous damage. The following are several methods used for early detection of damage due to HTHA.

-Phased Array Ultrasonic Testing

-Time of Flight Diffraction Testing



-Field Metallographic Replication

Standards

API RP 941, Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants provides a guide for material selection and operator instructions for safe use of hydrogen at high temperatures.
API RP 571, Damage Mechanisms Affecting Fixed Equipment in the Refinery Industry identifies materials of construction that are not susceptible to HTHA.

Case Study

A well-known incident took place in April of 2010 at the Tesoro refinery in Anacortes, Washington. A tube rupture occurred in a 40-year-old carbon steel heat exchanger due to damage from HTHA overtime. The heat exchanger was operated outside of the hazardous region of the Nelson Curve as identified in API 941; however, it still suffered catastrophic failure due to HTHA leading to an explosion and subsequent fire which caused seven fatalities.

The CSB proposed several recommendations to the American Petroleum Institute (API) to help prevent future incidents related to HTHA as they deemed there to be significant risk of further incidents in the industry. They made the following recommendations:

- Clearly establish minimum necessary “shall” requirements – the current language of “should” is not adequate.
- Require the use of inherently safer materials
- Require verification of actual operating conditions to confirm adequate material selection
- Prohibit using carbon steel in processes that operate at over 400 F and 50 pisa partial pressure of hydrogen.

Result

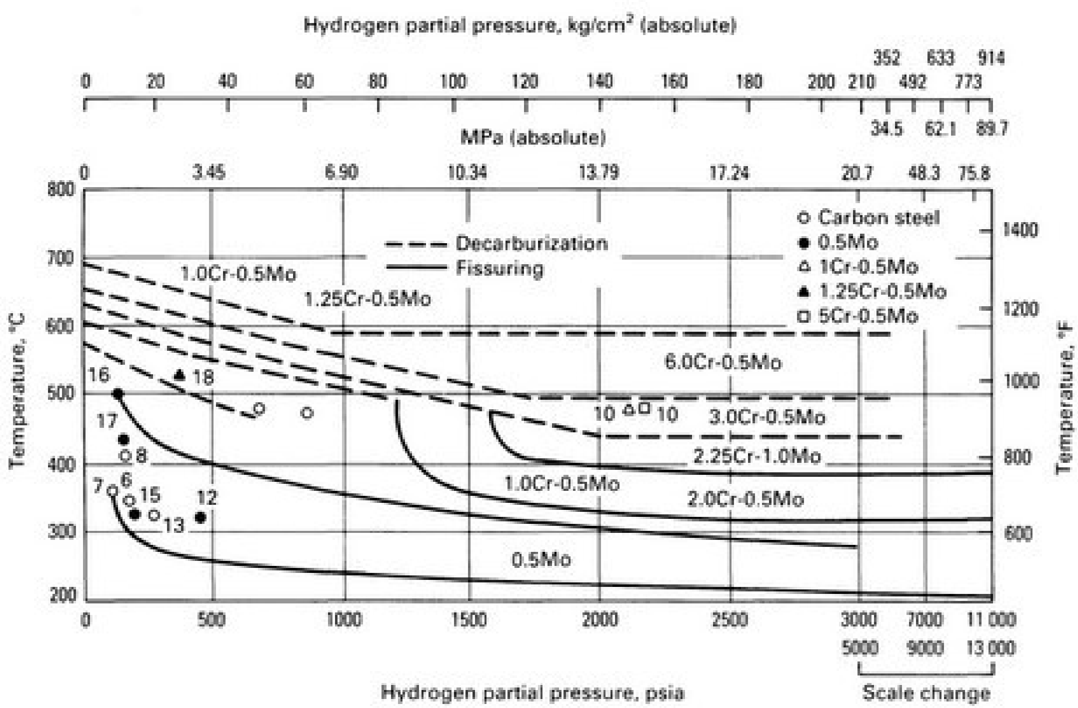
As a result of the investigation and recommendations made by the CSB, the API released the 8th edition of RP-941 in 2016. This edition included updates related to material selection, testing and operating suggestions for high temperature hydrogen operations and was updated to include a new, lower Nelson Curve, for non-post-weld heat treated carbon steel.

CSB Safety Alert

Because API did not implement the CSB’s recommendations to their expectations, the CSB released the following industry guidance to avoid HTHA equipment failure.

CSB Safety Guidance to Prevent HTHA Equipment Failure:

1. Identify all carbon steel equipment in hydrogen service that has the potential to harm workers or communities due to catastrophic failure;
2. Verify actual operating conditions (hydrogen partial pressure and temperature) for the identified carbon steel equipment;
3. Replace carbon steel process equipment that operates above 400 °F and greater than 50 psia hydrogen partial pressure; and
4. Use inherently safer materials, such as steels with higher chromium and molybdenum content.



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