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PRACTICAL EXPERIENCE IN THE EARLY DETECTION AND ASSESSMENT OF VESSELS WITH HTHA DEGRADATION

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Abstract

High Temperature Hydrogen Attack (HTHA) is a damage mechanism with a significant impact in the refinery industry, internationally. The mechanism results in gradual and relatively slow degradation of the vessel material during the incubation time period, but more rapid degradation thereafter. The paper gives an overview of this damage mechanism in the context of inspection surveys to identify degraded areas, and engineering assessments to assess fitness for continued service. The basic mechanism of HTHA is described, with reference to the influence of temperatures and pressures. The various forms of attack, as well as the process of HTHA degradation, and the influence of a number of factors, are described. The detection of attack using advanced NDT and risk-based approaches are described. Available inspection techniques for HTHA detection and quantification are reviewed. Specific attention is given to Advanced Backscatter, Velocity Ratio, and Metallurgical Replication and Fast Fourier Transformation techniques. Typical reporting formats are presented. Practical examples regarding the mapping of the survey results for a specific vessel are given. The Fitness For Service (FfS) and Remaining Life assessment of equipment with identified damage, is discussed in the context of the API RP 579. The alteration and rerating of equipment that has suffered from HTHA are considered when FFS of HTHA equipment, is discussed

1. Introduction

High Temperature Hydrogen Attack (HTHA) is a damage mechanism with a significant impact in the refinery industry, internationally. The mechanism results in gradual and relatively slow degradation of the vessel material during the incubation time period.. Recent experience have indicated that combinations of the material of construction and operating conditions normally believed to be immune to attack, are indeed susceptible. This paper gives an overview of this damage mechanism in the context of inspection surveys to identify degraded areas, and engineering assessments to assess fitness for continued service.

2. Basic Mechanism of high-temperature hydrogen attack

At elevated temperatures (above abut 400 °F (204 °C)), hydrogen molecules (H_2) dissociates into the atomic form (H), with the result that the very small hydrogen atom (0.05 nanometre diameter) can readily diffuse into carbon steels. High partial pressures and operating temperatures accelerate diffusion. The diffused hydrogen can interact with certain components of the steel microstructure, resulting in damage to the material of construction. The nature of the damage encountered can be classified into a number of forms of attack observed.

3. Forms of attack observed

3.1 Surface decarburisation

At relatively low hydrogen partial pressures, and elevated temperatures, the diffusion of hydrogen atoms is relatively slow and only penetrates the surface layer. Here the hydrogen reacts with carbon–rich micro-constituents (such as Fe_3C), thus removing carbon from the microstructure and resulting in a decarburised (low-carbon, weak) zone.

Surface decarburisation has a very small consequence on asset integrity, at most, it reduces the strength of a thin surface layer. The other forms of degradation, notably internal fissuring, have a much more pronounced effect on asset integrity.

3.2 Internal decarburisation and fissuring

Lower operational temperatures (but above 430 °F) and high hydrogen partial pressures favour *internal* decarburisation, as the hydrogen penetrates deeper and attacks micro-constituents beyond the surface layer, followed by fissuring. The consequence of the reaction between the hydrogen and carbon is that methane forms, which cannot escape to the surface, due to its relatively large molecular size. The methane accumulates at grain boundaries, and cause high localised stresses. Small (10 to 100 micron) cracks or fissures form, separating the grains. These fissures can link up to form cracks, threatening the integrity of the unit.

4. The HTHA Damage Process

The HTHA damage process progresses through three distinct stages:

1. The incubation period, when changes cannot be detected. During this period, methane pressure builds up without causing significant damage. Voids which are microscopic in size, form. Empirical curves exist which indicate the incubation time for several steels at operational conditions.
2. Rapid fissure formation and growth, with rapid property deterioration. During this phase, the micro-voids join up to form fissures and cracks.
3. The terminal stage, when carbon is exhausted and materials properties stabilize on the final, deteriorated level.

5. The influence of steel composition

Carbide Forming alloy elements, such as Cr, Mo, V, Nb, Ti, reduce the tendency to internal fissuring, due to its stabilising influence on internal iron carbides. At a hydrogen partial pressure value of 6.9 MPa, absolute, for example, no HTHA attack is expected for carbon steels at temperatures of 500 °F, and lower. For 1.25 Cr 0.5 Mo steels at the same pressure, however, no HTHA attack is expected at temperatures up to 975 °F. These inter-relationships between steel type, hydrogen partial pressure, temperature, and forms of HTHA attack, are summarised on curves developed by G.A. Nelson, and referred to as Nelson Curves. The first of these curves were developed in 1949, and have provided satisfactory guidance for many years. However, longer-term exposure showed damage in C–0.5 Mo and Mn-0.5 Mo steels, at operational conditions below the appropriate C-0.5 Mo immunity lines. The latest guidelines for these steel types indicate that the carbon steel immunity line should be used as the guideline to establish C–0.5 Mo and Mn-0.5 Mo susceptibility.

6. Stress and HTHA

6.1 Primary Stresses

The Nelson curves have been drawn up on the basis of steels operating at stress levels not exceeding the limits imposed by Section VIII, Division 1 of the ASME code. No cases of observed damage of units operated below the Nelson Curves have been attributed to primary stress levels exceeding the Division 1 requirements. Experience with units designed to Division 2 has similarly been excellent.

6.2 Secondary and Peak Stresses

HTHA cracks have been observed in highly stressed regions of otherwise resistant material. High thermal stresses, localised cold work, stress concentrators and welding residual stresses have been identified as factors which can accelerate HTHA attack in local regions, through high levels of secondary and peak stresses, and must obviously be avoided as far as possible.

7. Reduction of susceptibility

7.1 Postweld Heat Treatment

Post-Weld Heat Treatment (PWHT) reduces residual stresses in welded joints and, as such, has a positive effect on reducing HTHA susceptibility in the region of welded joints. In addition, PWHT improves HTHA resistance by stabilising the carbides. Furthermore, PWHT at the maxima of the allowable PWHT range of temperature and time, has been shown to be beneficial compared to standard PWHT, for 1 Cr-0.5 Mo, 1.25 Cr- 0.5 Mo and 2.25 Cr-1 Mo steels.

7.2 Cladding

Cladding the internal surface of a vessel with a sound, metallurgically bonded austenitic stainless steel cladding or weld overlay, has been shown to improve HTHA resistance significantly. Diffusion of hydrogen in austenitic stainless steel is approximately two orders of magnitude lower than that in ferrous steels, with the consequence that the internal surface of the vessel is effectively “shielded“ by the cladding. Cladding and overlays can however deteriorate, and one case of HTHA attack of the base metal has been reported due to intergranularly cracked cladding.
Although cladding has beneficial effects, it is however not advisable to take credit for the presence of cladding when considering HTHA susceptibility at operational conditions.

8. Engineering FFS assessment and Remaining Life

When HTHA flaws are discovered through inspection, fitness for continued service must be assessed by using a practice such as API RP 579. The method of assessment will depend on the nature of the discovered flaws. In the case of decarburisation and micro-fissuring, the depth of the affected layer has to be established through NDT. The structural integrity of the unit, based on the properties of the unaffected remainder of the wall, will be assessed using the methodology of Section 4 (General Wall Loss). If cracks are evident, the cracks have to be sized and assessed using Section 9 of the Recommended Practice.

When remaining life is considered, the significant fraction of the service life required for incubation, has to be taken into account. at the stage of assessment, undetected attack may be present in the "unaffected area". Frequent monitoring, surface cladding and rerating are measures that can be considered in such cases.

9. Detection of HTHA

Material degradation caused by high temperature hydrogen damage occurs in three distinct stages. During the first stage hydrogen reacts with carbides located in the material leading to decarburisation and the formation of methane bubbles located at the grain boundaries.

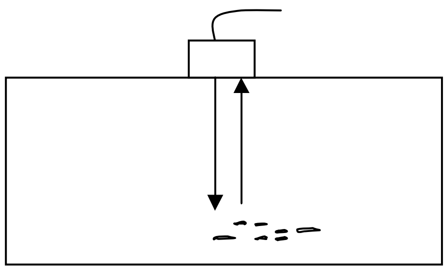
With time the methane bubbles will lead to micro-cracks, stage two, which, affect the mechanical properties of the material, these micro-cracks can propagate, stage 3 and may lead to failure.

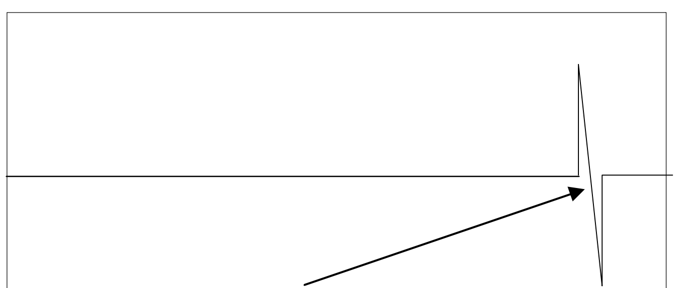
Detection of HTHA is reliably performed non-destructively using advanced back scatter ultrasonic techniques early during the stage 2 degradation.

There is no "correct" way to approach the detection of HTHA; it is a function of the philosophy of the plant and specific equipment risks. The most cost-effective and often specified approach involves the advanced backscatter ultrasonic technique which includes the following and is appropriate for detection and assessment:

- Backscattering
- Velocity Ratio
- Fast Fourier Transformation (Spectrum Analysis)

The advanced ultrasonic back scatter technique is based on the detection and subsequent analysis of the backscattered ultrasonic signal. Clearly as the size of the micro-cracks increase the amount of energy reflected increases and the amplitude of the reflected signal increases proportionally. As the micro-cracks develop deeper into the material the depth of penetration can be measured and monitored. Interpretation must however rely on the pattern rather than the absolute backscattering amplitude in order to differentiate between HTHA and inclusions and impurities.





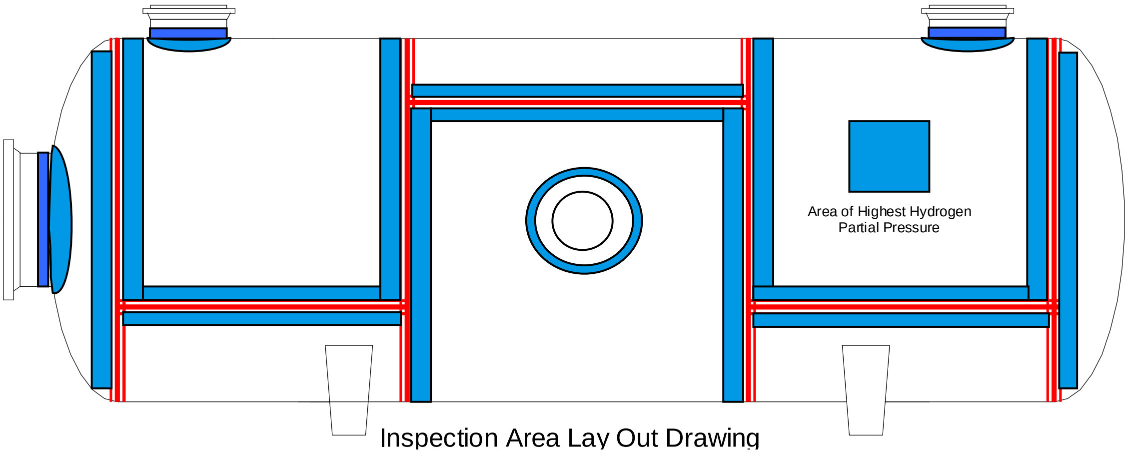
The primary detection technique is the pattern based back scattering technique and involves the use of a normal UT flaw detector with a 0 degree, 1/2", 5Mhz broadband, longitudinal wave transducer. Suspect areas are scanned and the ultrasonic signal shape is observed for evidence of "scatter" from the grains as depicted in Figure 1.

The purpose of the inspection technique is to reliably detect the presence of micro-cracking as well as accurately and effectively measure and report the depth of penetration such that this information can be used to determine fitness for service and remaining life.

The exact technique deployed as the primary detection technique is dependent on whether the parent material or welds are to be inspected. None the less the primary detection tool is the advanced backscatter ultrasonic technique supported by the velocity ratio and Fast Fourier Transformation techniques both of which are used to support the backscattering technique.

10. Inspection Planning and the use of Advanced NDT

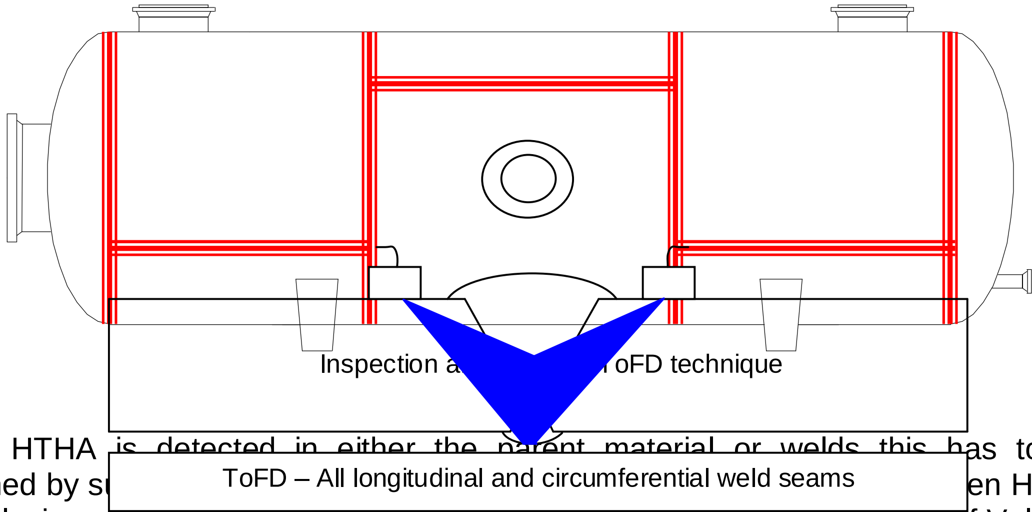
An initial assessment of the vessel will identify susceptible regions of equipment. Generally on a process vessel the inspection would consist of inspecting a band 50mm wide on either side of all longitudinal, circumferential or nozzle to shell welds, as well as an area of 1m X 1m at the area of highest hydrogen partial pressure. Further to the above all longitudinal and circumferential welds are also inspected using the Time of Flight Diffraction ultrasonic technique with steep angle transducers.



Inspection Area Lay Out Drawing

10.1 Backscattering

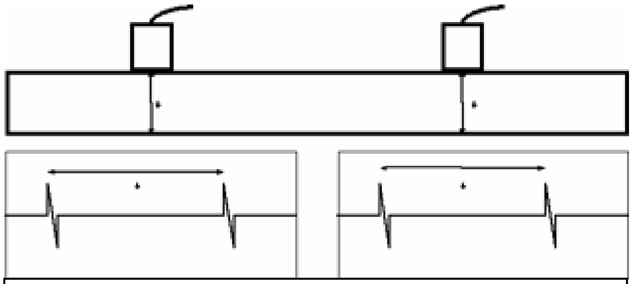
A 50 mm wide band on either side of all longitudinal, circumferential and full penetration nozzle welds as well as a 1m² area of the shell material at the location of the highest operating temperature and hydrogen partial pressure.



Where HTHA [illegible] has to be confirmed by s[illegible]en HTHA and inclusions or other impurities. This is a two step approach and consists of Velocity Ratios and Fast Fourier Transformation techniques. Where no evidence of HTHA is detected by the primary inspection technique the inspection is considered complete.

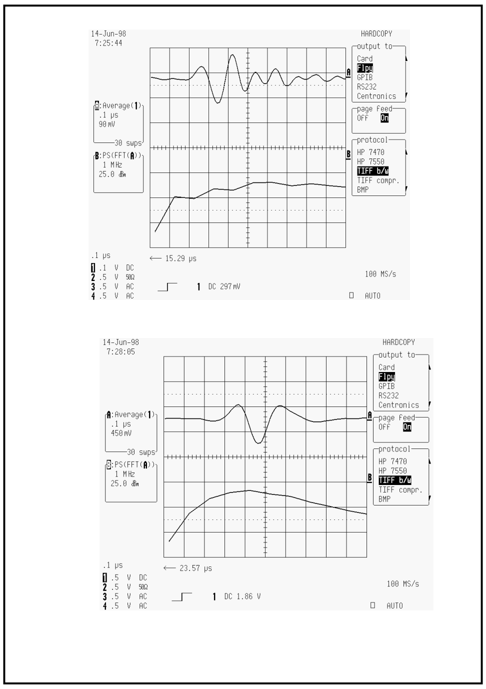
10.2 Velocity Ratios

This technique relies on measurement of transit times and can be accomplished with a conventional digital UT flaw detector. A 5 MHz 0º broadband compression wave and 0º broadband 1/2” 5 MHz incident shear wave is used for measurement of transit times. Special viscous couplant is used for the 0º incident shear wave to transmit the ultrasonic energy. Using the same spot location first the longitudinal velocity and then the shear velocity is measured on the basis that the thickness does not change in that location. The ratio of VS/VL should be <0.55. Ratios above this value are an indication of HTHA and if this is found the Fast Fourier Transformation technique is used.



Measurement of Velocity Ratios

10.3 Fast Fourier Transformation



Specific equipment in the form of an oscilloscope and pulser/receiver, with the added requirement that the oscilloscope be equipped with signal averaging and Fast Fourier Analysis is normally required although this can be performed on any computer with the required software as long as the "A" scan can be averaged, digitized and saved. A 10 Mhz, 0.375" broadband compression wave transducer is used for spot measurement. No

Special couplant is required. The theory is that at the higher frequencies there is greater attenuation when a sample has HTHA, 8Mhz is the nominal frequency selected as the point to assume measurement. An "A" scan is collected over the effected area and digitized and averaged, the signal is then processed using Fast Fourier Transformation and the result analysed.

10.4 Material replication

Material replication and scoop sample analysis can be used to aid in the understanding of the stage of damage. Scoop samples, analysed in a SEM at ~ 15000x magnification, can detect the voids which signify the early stages of attack. Metallurgical replica's, can normally only detect the advanced stages such as fissuring and decarburisation.

11. Conclusions

HTHA is a damage mechanism with significant relevance in the Refinery Industry. The slow progress of the mechanism at first, combined with the rapid acceleration after the incubation period, makes it a dangerous mechanism if not detected early. Inspection and NDT strategies can and must be focused on units and locations of high risk, and can be performed unobtrusively. The combination of a risk – based approach and advanced NDE will ensure the early detection and effective mitigation of damaged assets.

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