High temperature hydrogen attack (HTHA) is a damage mechanism that has the potential to cause catastrophic failure of low alloy steel processing plant. This was tragically illustrated by the incident at Tesoro Anacortes Refinery in the USA in April 2010 which resulted in the death of seven people. The control of HTHA is addressed at the time of equipment design through the procedures described in API 941 “Steels for Hydrogen Service”. This recommended practice is based upon experience and has undergone modification following reported cases of damage in materials operating under conditions previously believed to be safe. The API risk based inspection recommended practice API 581, contains a module that allows the risk of HTHA to be assessed. Both these codes indicated that the material of construction and the operating conditions at Tesoro Anacortes Refinery were acceptable. The subsequent incident report issued by the U.S. Chemical Safety and Hazard Investigation Board in May 2014 has made significant recommendations to reassess the operating conditions under which carbon steel may be operated in hydrogen service. If adopted, these recommendations will result in significant changes to the management and inspection requirements of such carbon steel equipment. This paper reviews the findings of the Tesoro Anacortes incident report and describes the impact that adoption of the U.S. Chemical Safety Board recommendations will have on the requirements for inspection to ensure integrity of carbon steel equipment in hydrogen service and the syngas industry.

1. INTRODUCTION

In April 2010, the failure of a heat exchanger in hydrogen service led to the death of seven people. The subsequent investigation by the U. S. Chemical Safety and Hazard Investigation Board (CSB) concluded that the damage mechanism was High Temperature Hydrogen Attack (HTHA). This conclusion meant that damage had occurred under conditions that would normally be considered at low risk of attack. Recommendations were by CSB made that, if adopted, would mean that a large amount of carbon steel equipment and pipework in hydrogen service would be considered at risk of HTHA. This paper reviews the CSB report and discusses the implications for risk based inspection of equipment in hydrogen service.
2. THE PROCESS

The unit operation within the Tesoro Anacortes refinery where the failure occurred was a naphtha hydrotreater (NHT). This unit uses hydrogen to react with contaminant species in the naphtha to a form compounds that can be subsequently separated from the naphtha process stream. The hydrogen and naphtha feed is heated in a series of heat exchangers on the tube side, before passing to a furnace and then the NHT reactor. The treated stream is then passed through the same heat exchangers on the shell side, cooling the process gas and pre-heating the feedstock. A schematic illustration of the arrangement is shown in Figure 1.

Fig.1 Schematic illustration of the Anacortes Tesoro NHT unit also showing the location of the rupture (Source: US Chemical safety Board Report 2010-01-I-WA, May 2014)

As shown in Figure 1, there were two parallel banks each containing three heat exchangers. The two banks could be operated independently to allow periodic decoking to be undertaken. At the time of the incident, bank DEF was in operation. Unfortunately, at this time, technicians were working on bank ABC in preparation to bring it on line.

The operating conditions are shown on Table 1. The inlet and outlet operating conditions of the heat exchanger banks were monitored but intermediate temperatures or pressures within the individual exchangers were not measured or recorded.
Table 1: Nominal operating conditions (CSB report)

<table>
<thead>
<tr>
<th></th>
<th>Temperature °C</th>
<th>Pressure MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Tube Side</td>
<td>50</td>
<td>4.4</td>
</tr>
<tr>
<td>Outlet Tube Side</td>
<td>288</td>
<td>4.3</td>
</tr>
<tr>
<td>Inlet Shell Side</td>
<td>330-375</td>
<td>4.1</td>
</tr>
<tr>
<td>Outlet Shell side</td>
<td>130</td>
<td></td>
</tr>
</tbody>
</table>

3. THE HEAT EXCHANGERS

The top heat exchangers (A in bank ABC and D in bank DEF) experienced the highest temperatures. At the time of construction, it was recognised that at the higher temperatures experienced by the exchangers, that HTHA was a possibility. To mitigate this, exchangers A and D were constructed from Carbon-½Mo steel (SA-302-B) and overlaid with 316 stainless steel. The remaining exchanger shells were constructed from carbon steel (SA-517-70) and the hottest part of the shell in exchangers B and E were also clad with 316 stainless steel. Figure 2 shows the construction of the shells divided into sections described in the US CSB report as “cans” joined by circumferential butt welds.

Figure 2 shows the fabrication layout for exchangers B and E. Can 4 was clad with 316 stainless steel and the cladding started immediately after the weld connecting Can 4 to Can 3.

It was noteworthy that the construction welds in the shell of these exchangers were not post weld heat treated.
4. THE FAILURE

During operations being undertaken to bring the ABC bank of exchangers on line, the D exchanger shell catastrophically ruptured. The ruptures occurred along weld seams as can be seen in Figure 3.

**Fig.3** The DEF bank of exchangers following the catastrophic failure of exchanger E. (Source CSB report)

The subsequent investigation found that:

- The failure occurred due to High Temperature Hydrogen Attack.
- The main failure occurred in the circumferential weld connecting Can 3 to Can 4. This weld was the hottest weld that was not clad with stainless steel.
- Other welds in Exchanger B suffered similar damage.
- HTHA and cracking damage was only observed in the heat affected zones (HAZ) of welds. Parent material appeared unaffected.
- The material in Exchanger D may have been affected by the fire following the failure.
- Exchanger B in the other bank ABC, had similar damage to that observed in Exchanger E. The material of Exchanger B was not affected by the heat of the fire following the failure and served as an “exemplar” heat exchanger representing the condition of Exchanger E prior to the failure.
- HTHA damage typically manifests itself as fine micro-fissuring which requires specialist inspection techniques for detection. In the B heat exchanger, classic HTHA was observed but large fissures in the weld were also found (Figure 4).
- Metallurgical examination of the welds showed the hardness of the parent material and the weld HAZ was mainly in the range 80 to 100 HRB. In some HAZ areas, higher hardness close to 22 HRC was observed.
- The material analysis suggested that the carbon steel weld HAZ would have a moderate susceptibility to hydrogen induced cracking (this would normally require controlled weld procedures to avoid the risk of hydrogen cracking).

Fig. 4 Crack found in HAZ of weld between Cans 3 and 4 in Exchanger B (Source: Appendix to CSB report, Inspection report by Spectrum Inspection)

The metallurgical report concluded that the damage was significantly dominated by HTHA but other mechanisms such as Hydrogen Induced Cracking made a contribution.
5. HIGH TEMPERATURE HYDROGEN ATTACK

The damage mechanism that leads to HTHA is:

- Dissolution of hydrogen from the process environment.
- Decarburisation caused by the reaction between carbon (as carbide) and dissolved hydrogen to form methane.
- Fissuring and cracking caused by internal methane pressure.

An example of damage caused by HTHA is shown in Figure 5.

Fig.5 Micro-fissures in Carbon \( \frac{1}{2} \text{Mo} \) steel caused by HTHA

The risk of HTHA occurring is influenced by temperature and hydrogen partial pressure. Increasing both these factors increases the risk of damage. Traditionally, material selection for hydrogen service is controlled by the application of API RP 941 “Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants”. This recommended practice provides graphical representations of the Nelson Curves that define the “critical” condition for HTHA to occur. For conditions falling above the curve, HTHA is a risk. Below the curve, HTHA is considered unlikely to occur. It is important to note however, that these curves are created by observation; they separate the examples of operating conditions that have led to HTHA from those operating conditions that have not. An example of the Nelson Curve diagram taken form API 941 is shown in Figure 6.
The individual curves shown in the Nelson Curve graph in Figure 6 refer to the candidate steels for hydrogen service ranging from the lowest curve for carbon steel to the uppermost curve that applies to 3Cr-1Mo steel.

In addition to the Nelson Curves, API 581 “Risk Based Inspection Technology” contains a module for the assessment of HTHA. This approach depends upon the calculation of a parameter $P_v$ which depends upon the hydrogen partial pressure, temperature and time in service.

The Nelson Curve approach takes no account of the time in service. The Nelson Curves are supposed to provide guidance as to the conditions that will cause no attack. API RP 941 does however; provide information as to expected time for incipient attack of carbon steels operating above the Nelson Curve.

Dependent on the calculated value of $P_v$, the various steels can be characterised as high, medium low and not susceptible to HTHA. These categories are then used to assign damage factor risk levels. The assessments undertaken for the B and E exchangers at Tesoro Anacortes Refinery concluded that they had a low susceptibility to HTHA.

As noted above, the actual operating temperatures of the intermediate B and E exchangers were not known from any in service monitoring equipment; the temperature at the area of failure could only be inferred from inlet and outlet temperatures from the heat exchanger banks as a whole. The US Chemical Safety Board undertook detailed modelling of the heat exchanger operation to define the actual operating conditions at the damage locations in the B and E exchangers. Based on this modelling, they reported that the exchangers operated below the Nelson Curve in an area which would normally be considered safe. Examples of the results of this modelling are shown in Figure 7.
Fig. 7  Calculated operating conditions for the weld connecting Can 3 to Can 4 relative to the Carbon Steel Nelson Curve

As a result of this and similar modelling undertaken for other welds that experienced damage, The Chemical Safety Board has concluded that the present Nelson Curve for carbon steel is non-conservative and has recommended a modification to the curve as shown in Figure 8.

Fig. 8  Modification to the Nelson Curve for carbon steel recommended by the Chemical Safety Board
This effectively states that for any hydrogen partial pressure above 50 psia (0.35 MPa), any carbon steel pressure equipment operating above 400°F (204°C) is at risk of HTHA.

If this recommendation is adopted, much of the carbon steel equipment currently in hydrogen service in ammonia, methanol, refinery and related plants will be considered at risk of HTHA. This would typically lead to specific risk management plans and inspection for HTHA for equipment previously deemed not to be at risk.

6. DISCUSSION

Based on the metallurgical examination described by the CSB report, it would be tempting to conclude that API RP 941 and API RP 581 provide incorrect information. The CSB report critiques these recommended practices, commentating on the use of the word “should” denoting a recommendation as opposed to “shall” which refers to a requirement. However, both these standards are specifically described as “Recommended Practice” and neither claims to state rules by which HTHA should be managed. They do not guarantee freedom from HTHA and neither document makes this claim. Rather, they provide guidance as input to an organisation’s risk management plan. It is considered that many organisations take the view that if an item of equipment operates below the Nelson curve and/or is deemed to be at low risk or not susceptible according to API RP 581, then it is safe not to inspect specifically for HTHA.

This however, does not mean that inspection is unnecessary. A risk profile has been estimated for the Tesoro NHT heat exchanger shells and the results are shown in Figure 9. The two points indicate the estimated profiles for cases in which HTHA had been identified as a credible damage mechanism and the lower risk point for a case in which HTHA had not been considered to be active. Regardless, the level of risk, both cases to represent high or sufficient risk to trigger a requirement for inspection. While the CSB report notes the absence of inspection for HTHA it does not provide much information about what inspection was actually undertaken if any.
It is considered of particular relevance that the failed shell was not post weld heat treated. This should have been noted in any hazard or risk assessment and should have identified a need for inspection regardless of whether HTHA was identified as an active damage mechanism or not. The absence of post weld heat treatment would be expected to identify the possibility of Hydrogen Assisted Cracking (cold cracking of susceptible material in the presence of hydrogen sometimes called under bead cracking). This damage mechanism is indeed discussed in the CSB report since the damage observed was not classic HTHA and had many characteristics of hydrogen assisted cracking. Such cracking would typically be associated with hard welds and the Tesoro exchangers had hardness levels close to or below, the normally accepted threshold hardness of 22HRC. However, in highly stressed situations, under bead cracking may occur below this hardness level. Notably, all damage was located in HAZ material where weld residual stresses would be highest possibly as high as the material yield stress level. Neither API RP 941 nor API RP 581 include stress in their assessments. There is discussion in API RP 941 and its supporting documentation (Technical Basis Document for API RP 941) concerning stress and they do state that stress increases the likelihood of HTHA.

It is clear from both API RP 941 and API RP 581 that the risk of HTHA is strongly dependent on the operating conditions. The CSB report strongly makes the point that the actual operating conditions were not known for the intermediate exchangers B and E. Notwithstanding the process modelling that the CSB undertook following the incident, it was reported that the operating conditions within these exchangers varied as a result of coking of the tubes and the process demands of the refinery. Coking would be more likely at the highest temperatures i.e. in exchangers A and D (Figure 1). The effect of coking of the tubes would be to reduce heat transfer efficiency. This in turn would likely result in a reduction of the heat extracted from the treated process steam in the hottest exchangers A and D and an increase in the temperature of the downstream exchangers B and E. It is understood that no
process studies were undertaken to understand the actual process temperatures of the intermediate, or indeed any, of the exchangers. This observation emphasises the importance of process control and review as an input to a risk assessment. Consequently, the periodic hazard reviews that were undertaken failed to adequately take the actual operating conditions into account.

HTHA has been observed in steels nominally deemed to be operating in low risk conditions on other occasions. It is now well documented that Carbon-½Mo steels may perform very differently depending on the metallurgical condition. Normalised material has better performance than annealed and this is also documented in both API RP 941 and API RP 581. It would be naive to believe that the effect of metallurgical condition of the risk of HTHA was unique to Carbon-½Mo steels and that other steels including carbon steels were immune to this effect. The purpose of post weld heat treatment of carbon and low alloy steels is twofold. Firstly to reduce residual stress and secondly to modify the metallurgical condition i.e. soften the potentially hard martensitic structures that may form in the HAZ. It is distantly possible that those metallurgical structures in non-post weld heat treated HAZs make be more susceptible to HTHA than materials that have been post weld heat treated. It is noteworthy that no HTHA damage was observed in parent material remote from welds.

It is considered likely that the absence of post weld heat treatment contributed to an increased susceptibility to both HTHA and hydrogen assisted cracking. There have been other cases of HTHA occurring unexpectedly in non-post weld heat treated equipment. These are referred to in the CSB report and also by McLaughlin et al in their paper “Cracking of non-PWHT’d Carbon Steel Operating at Conditions Immediately Below the Nelson Curve” (2010 ASM Pressure Vessels and Piping Conference, July 201 Bellevue, Washington). In all cases reported, the damage occurred at welds.

The implication is that there is no need to modify the Nelson curves. Rather, the requirement is to take post weld heat treatment or that lack of it into account as part of the risk assessment. The CSB report makes the point that the effectiveness of post weld heat treatment cannot be guaranteed. While this is true, it is reiterated that that any risk assessment would be very unlikely to result in no inspection at all regardless of either HTHA or post weld heat treatment. These factors would potentially influence the frequency of inspection, not whether or not inspection was necessary.

It is considered that the recommendations made by the CSB targeted at the API standards API RP 941 and API RP 581 are not justified. The need to limit the temperature of all carbon steel equipment in hydrogen service to a maximum of 400°F (204°C) is thought to be over conservative. It is strongly recommended however, that any carbon steel equipment in hydrogen service that has not been post weld heat treated should be reviewed and inspection test plans created or modified to take into account the possibility of HTHA and hydrogen assisted cracking. Inspection for classical HTHA is a difficult and specialist technique. The identification of small internal fissures is not straightforward and requires advanced ultrasonic techniques dependent on signal attenuation and similar methods. In the case of the Anacortes Tesoro NHT exchangers however, the cracks prior to failure were exceptionally large. Any risk assessment that had identified HIC as a potential damage
mechanism would be expected to result in inspection test plans that would find such large defects.

The incident at Anacortes Tesoro and the subsequent CSB report do however, emphasise the importance of a comprehensive asset management programme. Risk assessment and inspection are vital parts but they do not in themselves, constitute a complete asset management programme. In the case of the Anacortes Tesoro incident, the value of process review, process control and management of change were all underrated. Of particular concern was an observation in the CSB report that reviews of the corrosion control programme were discontinued in 2006 since they were not a “legal requirement”. The asset management programmes that are required to keep modern industrial plants safe are not the domain of legislative bodies. They are the responsibility of the plant owners to maintain their plants safe as reasonably possible.

7. Conclusions

1. The failure and/or of the Anacortes Tesoro NHT exchanger was caused by High Temperature Hydrogen Attack in combination with a hydrogen assisted cracking mechanism that occurred only in the heat affected zones of welds that had not been post weld heat treated.

2. The recommendation to revise the Nelson curve does not appear justified given the influence that the lack of post weld heat treatment appeared to play.

3. The API documents API RP 941and API RP 581 are not intended to set rules by which HTHA is assessed and do not substitute for sound risk assessment activities and asset management that should draw upon these documents for advice.

4. It is considered that any reasonable risk assessment would have led to inspection test plans that called for inspections that would have detected the damage that occurred in the Anacortes Tesoro NHT exchangers. It would be expected that such a risk assessment would have identified the potential risks associated with the absence of post weld heat treatment.

5. Risk assessment constitutes one aspect of a comprehensive asset management program that is required to ensure safe operation of pressure equipment. Such an asset management program is the responsibility of the owners to put into place.

(Most of the illustrations and comments are reproduced from the US Chemical Safety and Hazard Investigation Board Report 2010-01-I-WA, May 2014. This report is available at http://www.csb.gov/tesoro-refinery-fatal-explosion-and-fire/)