Maintaining the integrity of process plant susceptible to high temperature hydrogen attack. Part 2: factors affecting carbon steels

Prepared by TWI Ltd for the Health and Safety Executive
Carbon steel process plant that operates with hydrogen at elevated pressure and temperature can be weakened by a phenomenon known as high temperature hydrogen attack (HTHA). Hydrogen diffuses through the steel and reacts with carbon to form methane which builds up and degrades the steel’s mechanical properties. If this phenomenon is taking place and continues undetected, it can potentially lead to failure of the process plant and a major accident. A fatal fire and explosion at the Tesoro Refinery in the USA in 2010 was caused by rupture of a hydrocarbon containing heat exchanger which had been weakened by HTHA.

HSE commissioned research to give a better understanding of maintaining the integrity of process plant operating in high temperature hydrogen service susceptible to HTHA. The research is described in two reports which should be read together. Part 1, RR1113, gives an analysis of the performance limitations of ultrasonic non-destructive testing techniques when searching for the presence of HTHA, and emerging technologies that may offer improved detection. Part 2, RR1114, discusses factors affecting HTHA for carbon steels including: the safe operating pressure and temperature envelope for plant (‘Nelson Curves’); steel type, welds, stress and other material factors; and equipment operating history.
Maintaining the integrity of process plant susceptible to high temperature hydrogen attack. Part 2: factors affecting carbon steels

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This is the second of two reports on maintaining the integrity of process plant operating in high temperature hydrogen service. The two reports should be read together.

This second report is RR1134 ‘Maintaining the integrity of process plant susceptible to high temperature hydrogen attack. Part 2: factors affecting carbon steels’.

The first report is RR1133 ‘Maintaining the integrity of process plant susceptible to high temperature hydrogen attack. Part 1: analysis of non-destructive testing techniques’.
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1 **Introduction**

Following a catastrophic fire at the Tesoro Anacortes Refinery, USA, in April 2010 (the ‘Tesoro incident’), the US Chemical Safety and Hazard Investigation Board (CSB) issued a strongly worded Safety Alert, prohibiting the use of carbon steels that operate above 400°F (204°C), 50psia (3.5bar) hydrogen partial pressure \([H_2]\). It was stated that “…inspections should not be relied on to identify and control HTHA, as successful identification of HTHA is highly dependent on the specific techniques employed and the skill of the inspector, and few inspectors were found to have this level of expertise.”

If the recommendations of the CSB safety alert were to be applied rigorously in the UK, the cost to Industry would be anticipated to be very significant and considerable resistance from users likely. Nevertheless, the consequences of an equipment failure could be very severe. The HSE therefore require a thorough understanding of the current technical situation, so that a proportionate and safe position can be sought.

In order to provide information to the HSE concerning the conditions appropriate for application of carbon steel refinery equipment in high temperature hydrogen service, a review of the literature has been carried out to understand more clearly the likely reliability of the Nelson curves and the factors that can aggravate HTHA.

This report was generated in parallel with a sister report that examines the non-destructive techniques (NDT) for HTHA (Nageswaran, 2018).

2 **Objective**

The objective of this report is to provide HSE with a state-of-the-art understanding of HTHA for carbon steels. This is intended to inform the communications of HSE with industry, and to assist with decisions on any safety alert that HSE may issue.

3 **Approach**

A largely desk based exercise has been carried out to develop sufficient understanding of a number of contributing factors to assist ranking of the risk of failure of carbon steels due to HTHA in refinery equipment. The reliability of the existing Nelson curve was considered by examination of the available evidence.

A search of the published literature was carried out using search engines available to the TWI Library Services and references judged to contain pertinent information were acquired. A small amount of interaction with industrial representatives and bodies concerned with the phenomenon was had to improve the industrial relevance.

The review starts by examining the Tesoro incident that instigated the work before moving on to look closely at the API RP 941 standard that is the current go-to document relevant to HTHA. The effect of process and metallurgical variables are then examined in the context of their effect on HTHA.
4 Tesoro Anacortes refinery incident and the CSB Report

4.1 Introduction
It is worth examining the Tesoro incident here, as much of the concern surrounding carbon steel in high temperature hydrogen service today, stems from this incident. Pargeter (2016), carried out an initial assessment of the CSB report (CSB, 2014). Here, further details of the process units in question and the investigations that took place after the failure, reported by the CSB are scrutinised. Points that are relevant to the performance of carbon steel in high temperature hydrogen service are drawn out.

4.2 Background to the incident
The incident involved an explosion that fatally injured seven employees, following the catastrophic rupture of ‘heat exchanger E’ within the Naptha Hydrotreater Unit (NHU) at the Tesoro Anacortes Refinery, Washington. This happened in April 2010, only 38 days after a process hazard assessment (PHA) of the unit took place. This PHA was carried out in response to a previous Process Safety Management (PSM) and Risk Management Plan (RMP) compliance audit (carried out in 2007) that indicated that previous PHAs “lacked sufficient detail and did not identify all of the hazards of the process”. A number of other causal findings to do with inadequate PHAs, poor safety culture, and lack of regulatory safeguards were subsequently highlighted, with parallels being drawn with the CSB findings for the Chevron Richmond Refinery incident in 2012 (CSB, 2015). The incident is also notable as the only catastrophic incident of a unit investigated by the CSB to have taken place shortly after (1 year) an audit conducted in accordance with the federal U.S. Occupational Safety and Health Administration’s (OSHA’s) refinery National Emphasis Program (NEP). The foregoing demonstrates that there was a degree of complacency inherent in the approach taken within the refinery, but also that despite scrutiny from the safety authorities, the hazards connected to the unit were not investigated thoroughly enough to prevent the failure.

The metallic degradation mechanism associated with the failure was identified as HTHA, which is endorsed by TWI after reviewing the metallurgical reports available. A contributing factor in this case was identified as high residual stresses in as-welded (non-PWHTed) joints.

The CSB (2014) highlighted that there was no direct monitoring of the temperatures and pressures of the failed exchanger unit and so used computer modelling to estimate the operating conditions. The results of the modelling exercise indicated that the ruptured region was operating at temperatures and pressures below the Nelson curve for carbon steel according to API RP 941 (pre 2016 editions). It was thus asserted that the carbon steel Nelson curve could not be relied upon, in its then current form, to prevent HTHA damage or failure. The associated CSB recommendations to the API were to revise relevant standards to (in summary): prohibit the use of carbon steel in HTHA-susceptible service, require verification of actual operating conditions, revise the minimum requirements to prevent HTHA failures, and require inherently safer design. It is taken that the words require and prohibit indicate mandatory syntaxes are to be used in the standards, i.e. ‘shall’ instead of ‘should’.

Concerns over the actual temperatures, the inadequacy of the Nelson curves and the effects of welds deserve further interrogation as they potentially unsettle the ground upon which many plants are operating today.

4.3 Description of Tesoro naptha hydrotreater equipment and materials
The naptha hydrotreater unit (NHU) contained two banks of heat exchangers. These were designed to use the waste heat from the reactor, where impurities in the gas stream were removed by reaction with hydrogen, to pre-heat the feed (a mixture of naptha and hydrogen). There were three exchangers in each bank with the respective suffixes A, B, C and D, E, F as shown in Figure 1. The effluent from the reactor ran into the shell section surrounding the tubes that contained the reactor feed mixture. The path of the effluent and feed are illustrated in Figure 1, showing that exchange units A and D are the first in line from the reactor vessel.
where the highest temperatures would be expected. This is reflected in the materials selection for A and D, which had a C-0.5Mo grade base metal and were fully clad in an austenitic stainless steel grade (Type 304). The second set, B and E, were partially clad in Type 316 (Can 4 closest to the inlet only) and had a carbon steel shell material. The exchangers were made up of four 'Cans' joined together with circumferential welds and each featuring a seam weld along its length. Regular damage mechanism hazard reviews (DMHRs, commonly called 'corrosion reviews') incorrectly assumed that the entirety of B and E were clad. The unit was originally constructed in 1972 and therefore had been in service for 38 years prior to the incident. At some point it was modified to achieve a 64% capacity increase, but it is not clear from the CSB report when this was done or whether any materials were changed or replaced. An element of doubt therefore remains concerning the actual age of the components, but it is plausible that no shell material in B and E were replaced during the lifetime.

4.4 Non-destructive examination (NDE) of the heat exchangers

No NDE inspections took place specifically targeting HTHA type damage prior to failure. It is not clear from the CSB report if any other NDE was carried out on the shell side for any other reason, prior to the incident and what techniques were used or locations examined if it were the case. According to CSB, 2014b, ‘Inspections are required by the state of Washington and the CSB investigation file contains documents that indicate that the heat exchangers were likely inspected per the state requirements.’ However, it is not clear what the state requirements are, and whether these involved NDE of any kind.

Following the incident, NDE inspections of vessels B and E, using various techniques, identified indications of cracking associated with all seam and circ. welds of Can 3 for both B and E. Notably the exemplar, exchanger B, featured a 48” (1220mm) long continuous flaw, running over most of one side of the circ. weld connecting Cans 3 and 4 (CS4), and a 30” (760mm) intermittent flaw along the seam weld of Can 3 (LS3), See Figure 2. It is judged likely that these flaws had not grown appreciably due to the incident and therefore were of a detectable size some time before the incident. Appendix J of the CSB report details the NDE carried out on the parent steel of Exchangers B and E. Backscatter and velocity ratio measurement techniques were used for areas remote from any welds. Backscatter signals were identified, which can indicate HTHA. The follow-up velocity measurements led to the conclusion that these indications were due to inclusions or “stringers” (colloquialism for MnS inclusions, which are typical microstructural features from the steel making process). However, no metallurgical work is presented to support the claim that the indications identified were indeed stringers. Metallurgical sections provided in the supplementary Beta report certainly showed evidence of plentiful inclusions in the parent plate near the welds.

4.5 Metallurgical analyses

Exchanger E and the parallel exchanger B were subject to metallurgical investigation following the incident. Both suffered from HTHA in the welded unclad regions, with a higher degree of attack towards the inlet side. Severe attack was identified in the welds of Can 3 (adjacent to the clad part - Can 4) for both exchangers, with less advanced attack present in the welds of Can 2. Attack was exclusively located at the ID and was highly localised at the HAZ with decarburisation localised to the crack path locations. The composition of the parent steel conformed to the grade specification A515 grade 70 and had the expected ferrite-pearlite microstructure. The welds were multi-pass arc welds. No reference to a welding procedure was presented in the CSB report.

Charpy toughness and tensile properties for the base materials agreed well with the typical results and specifications. Weld bend tests from an area where damage had been identified in the NDE testing (CS3 - LS2 intersection) and cracked during testing, indicated that flaws from in-service damage were present. Specimens from welds not found to feature damage (LS1-CS2 intersection) did not initiate visible cracks in the bend tests.
Both the CSB and Pargeter (2016) dismissed the possibility of pre-existing cracks due to fabrication hydrogen cracking, for the principal reasons that the cracks were not transgranular and only occurred at the ID.

4.6 Process monitoring of temperature and pressure

The CSB analysis of the DMHRs reveals that the design data were heavily relied upon instead of measured process conditions. In October 2008, a DMHR was carried out by Lloyd’s Register Capstone. The temperature and pressure values supplied by Tesoro process engineering during this exercise for heat exchangers B and E (Figure 31 of the CSB report) were as shown in Table 1.

It is not clear where these values came from, but it is clear that operating conditions were reported to be below those of the design values provided. Both the design and operating values provided are below the Nelson curve for carbon steel by more than 35°F. Significantly, they are not within 25°F, 25psi of the Nelson curve, which is the condition that triggered a rule to invoke or ‘require’ instrumentation, according to the HTHA inspection procedure used. Furthermore, there was no clarification, in the procedure, on how to determine whether this condition existed. It is also interesting to note that a single external surface temperature measurement of 455°F was obtained in 1998, at the inlet to either B or E. It is not clear why this measurement was taken, whether it was used to calculate internal temperatures, or how typical the operating conditions were at that moment in time.

According to the CSB report, process conditions (temperature, pressure, flow, and composition data) were available for the NHU streams entering and exiting the two banks of the NHU heat exchangers. The pressure and temperature monitoring points are illustrated in Figure 1. This Figure indicates that the temperature of the effluent could be measured at both ends of each bank of exchangers, but that pressure was measured only at the inlet to the tube side. A pressure relief valve, rated to 585psig, was installed downstream of the Exchanger E (presumably shell side effluent stream) and was found to be working following the incident by way of a field-test. The Figure shows a distinction between ‘control system instruments’ and ‘field instruments’. It is unclear what the distinction means, but it is likely that the control system instruments were continuously monitored, whereas the field instruments were for one off measurements. The only process monitoring conditions presented in the CSB report were for the tube feed inlet pressure and the tube outlet temperature during start-up of bank A, B, C after de-fouling operations. The tube outlet temperature and pressure ranges from the information reported during the three separate start-up periods identified in the CSB report are illustrated in Figure 3 along with those during the final start-up prior to the incident itself. Note that pressure data were not presented for the three historic instances in the CSB report and so the pressure ranges during the final start up were applied for those instances identified. The ‘maximum allowable working pressure’ for Exchangers B and E was 655psig (45barg) (at 650°F (345°C)) shell side and 700psig (48barg) (at 600°F (316°C)) tube side, (see Beta Report M10198-B showing the manufacturer’s plate). These values are also plotted in Figure 3, which shows that the range of tube outlet conditions for the three instances identified were within 700psig (48barg) allowable pressure, but above the 600°F (316°C) mark. The pressure rating at the higher temperature is not known, and therefore it is not clear whether the data features excursions above the nominal allowable limits.

The shell side effluent stream is not illustrated in the report at all and it is not clear if these data were examined. Presumably, the effluent temperature entering the bank of heat exchangers would have had a higher temperature than the feed exiting the bank, as the effluent is the fluid that is used to heat the tubes and feed within them.

4.7 CSB modelling of process conditions

As no direct measurement data were available for exchangers B and E, the CSB performed process modelling to estimate the operating temperatures and hydrogen partial pressures using process modelling software. Distributed control system (DCS) data from the years
2007-2010, including temperature, pressure and composition, were used as inputs into the model developed to reflect actual operating conditions. The report states that a total of 10 days operation were modelled from this period. It is not clear how those specific days were chosen and how the temperatures and pressures for those days compared with other days during that period or before 2007. The results of the analyses for the circumferential weld joining Can 3 and 4 (known as CS4) and for the coldest region where HTHA damage was identified (named as CS2 joining Cans 1 and 2 in the main Tesoro report) are shown in Figure 4. It is clear that CS4 could have been operating close to or at conditions on the Nelson curve during the 10 day period simulated and certainly would have surpassed the original design conditions. If this envelope is an accurate range obtained from a data sample for a limited period, it is plausible that the envelope over its 38 year history would surpass the Nelson curve due to a number of excursions above it. The relatively small sample size used by the CSB for modelling was also raised by the API in feedback on the draft report (CSB, 2014b), with no qualifying response or defence provided by the CSB. A point of detail concerning the P-T envelopes described is that there is no clarity on the time spent at different points within the envelopes defined. If it were known that most of the time was spent in the low temperature region, this would be more concerning in terms of the reliability of the Nelson curve. Furthermore, it is not known if the CSB applied an additional safety margin to their calculated window. As the thermal modelling plays a critical role in condemnation of the Nelson curve within the CSB report, it would be reassuring to see a more rigorous presentation of how the results were arrived at.

The operating temperature analysis included consideration of fouling with fouling parameters calibrated by matching actual operating conditions under (known) fouled conditions. The distribution of fouling was understood to have greatly affected the process conditions within exchangers B and E and a distribution that ‘best matched the overall documented observations of heat exchanger fouling’ were selected. The selection of this distribution has been criticised by McGovern, (2016) who asserts that ‘Essentially, all deposits form in the exchanger where the reaction mixture passes through the dry point. This is normally the hottest exchanger. As the hottest exchanger fouls, the heat transfer load moves to the middle and cold exchanger, increasing the shell temperature in both exchangers.’ This argument is also put forward by API in their feedback on the draft Tesoro report (CSB, 2014b). However, it is clear that if the CSB had assumed a different fouling distribution in spite of the evidence available, then this would be a difficult position to defend and the use of observations is re-affirmed in the CSB response to the API analysis. McGovern also points out that there was no consideration of possible hydrogen ‘hot stripping’ operations in the report. This is a practice commonly used to remove hydrocarbons from the reactor catalyst, and could potentially be of concern. This practice is not mentioned in the CSB report. McGovern’s overall analysis is that the envelope predicted by the CSB was narrow and that excursions above the Nelson curve were likely to have occurred.

The envelope defined for CS2 sits approximately 40°F, 20psi below that of CS4 and is 40°F from the Nelson curve at its hottest point. This region is therefore substantially below the carbon steel Nelson curve. It does, however, breach the new Nelson curve defined for welded carbon steel without PWHT shown in the 8th edition of API RP 941 issued in 2016. Examination of the metallurgical reports reveals that the evidence for the damage present in CS2 is not very convincing, but there is damage apparent in LS2 adjacent to the weld, shown in Figures 24-30 of the BETA report provided as a supporting document on the CSB website (M10198, TESORO LS2 AND LS2/CS2 TEE FINDINGS). Damage in the same weld in Exchanger B, did not appear to be as extensive (Beta Report M10198-B).

Due to damages identified to have occurred below the long-standing carbon steel Nelson curve, the CSB proposed new limits to prohibit carbon steel equipment operating at process conditions above 400°F (204°C), 50psia (3.5barg). However, the lines appear fairly arbitrary, vastly conservative towards the low pressure end and without any reasoned argument for the chosen values put forward within the report. As mentioned above, the latest edition with the new curve, would seem adequate as far as the Tesoro incident is concerned and is based on a number of other failures of carbon steel welds without PWHT. A caveat to this would be for the case where the operating conditions for the majority of the time were in the lower regions of
The envelopes defined by the modelling analysis. The proposed CSB limit would be a severe restriction that would preclude the use of carbon steel for many plants operating today.

The background and suitability of the Nelson curves in terms of avoidance of HTHA issues in plant is the subject of Section 5.

4.8 **TWI conclusions on the Tesoro report concerning the occurrence of HTHA damage**

Although there is reason to believe that the carbon steel Nelson curve may have been surpassed at times in the hotter regions of the exchangers where major damages were identified, there were certainly some regions featuring very minor HTHA damage, operating in a process window below the Nelson curve of the day. Therefore, the Nelson curve published prior to the 2016 edition is not considered completely reliable for the prevention of all damage due to HTHA in carbon steel vessels in all instances.

A number of points lead to the conclusion that the conditions of operation resulting in failure were not particularly extreme:

- The relative lack of HTHA identified in the parent material.
- The operational envelopes predicted to be below the carbon steel Nelson curve by the CSB modelling exercise.
- The long-time service life of the unit (38 years).
- Exchanger B survived despite large flaws due to HTHA being present along the welds, indicating low service stresses.
- The pressure relief valve downstream to the exchanger E did not operate at any point and was confirmed to be working.

Nevertheless, it is judged plausible that the real operating envelope for the failed welds was larger than that calculated by the CSB using a limited data set (10 days within the last 3 years of the units operation).

The main aggravating factor appears to be service duration and the presence of welds without PWHT. Raised stresses and carbon activity in the HAZ of non-PWHTed welds would be expected to increase the susceptibility of such welds to HTHA.

The 2016 edition of API features a new curve for non-PWHT carbon steel welds and demonstrates that all of the damaged areas found by NDE and metallurgical analysis could have been predicted with this curve and the CSB defined operational process envelope.

Direct measurement of the process stream at each exchange inlet and outlet would have provided better data for consideration during DMHRs where the risk of HTHA might have been considered.

Routine NDE inspection of the welds using the same techniques that were used in the investigation after the incident (PAUT) may have helped to prevent failure by identifying damages before they became critical. In this case a flaw close to the dimensions of those measured on the exemplar vessel – Exchanger B - would have almost certainly have warranted a repair or replacement.
5 API RP 941

5.1 The carbon steel Nelson curve in Figure 1 of the standard

The API RP 941 standard ‘Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants’, has formed the basis for materials selection and assessments for HTHA in industry since the first edition was published in 1970. It represents an industry perspective based on the work of G A Nelson, and before him J. Shuyten, both of Shell Oil. Nelson drew curves through ‘satisfactory’ plant data, plotted on temperature - pressure axes which included a safety margin of approximately 30°F (API TR 941, 2008), and hence the term ‘Nelson curve’.

Nelson revised the curves many times before the creation of the standard. However, most of these changes were to do with C-0.5Mo and alloy steel additions and the position of the carbon steel curve remained largely unchanged since he first presented it in 1949. It is notable that the first edition of API RP 941, 1970 featured a split in the curve separating ‘welded and hot bent’ carbon steels and those that were ‘not welded’, as did some of Nelson’s work prior to its publication, recognising that welds had a detrimental effect. This split was removed in subsequent versions of API RP 941, i.e. the ‘welded and hot bent’ curve in the 1st edition became the position of the ‘carbon steel’ curve in subsequent versions, see Figure 5. The split between numbers of attacked and non-attacked points in the different editions of the standard over the years is provided in Table 2. It is clear that the number of points has not changed significantly from the first edition.

A summary of the references for the 11 carbon steel data with conditions in a range that includes the Tesoro incident, i.e. below 700°F (371°C) and 700psi (48bar), is shown in Table 3 and Figure 6. The position of the carbon steel curve and the data points in this region did not change from the first edition to the current 2016 edition of API RP 941, apart from an additional point (33s - a failure above the curve) and some re-numbering of the reference order.

There are no details regarding PWHT for the data points in editions published prior to 2016. It is highly likely that some of the data used to construct the previous carbon steel Nelson curves were for constructions made without PWHT or with poorly executed PWHT. Pressure vessel codes typically stipulate a maximum thickness allowable without PWHT for different materials (typically 1-1.5” for carbon steel). Awareness of the detriment of residual stresses and untempered microstructures to structural integrity was not widespread in the early days of pressure vessel manufacturing, when some of the earlier issues were encountered.

It is notable that only a few of the data points have any description of the specifics such as failure position relative to welds and duration to failure provided in the standard. This makes further interpretation and validation of the curves difficult. Any background data that Nelson kept were probably lost after the closure of his workplace – Shell Emeryville - in the 1970’s, but for a small package passed to the API by his widow, which contained very little data (API 2008a).

However, five of the data points in the range of interest do have references to papers in the literature these are:

Point 11 – Zapffe, 1944
Point 16 – Evans 1948
Point 19 – Ciuffreda and Rowland, 1957
Point 26 – Moore and Bird, 1965

These papers are summarised in subsections 5.1.1-5.1.4
5.1.1 Point 11 - Zapffe, 1944

The reference is a large document arguing the role of hydrogen in the failures of steam boilers, but draws on work performed under conditions relevant to hydrocarbon processing and HTHA. Images showing the decarburised surface of a specimen and attack along grain boundaries after 2 years at 400psi (28barg), 572°F (300°C) are shown, but is it not clear if these are from the authors own work or one of the many others drawn on in the article. Private communication with a K. G. Jones points out that decarburisation was expected at >400 psi (28barg), >390°F (200°C). HTHA due to production of soluble hydrogen from ammonia is also identified and temperatures of >390°F (200°C) again were identified as problematic. More worryingly, the author refers to work by Newitt and Inglis and Andrews, where temperatures as low as 390°F 200°C (in “comparatively short term tests”) and 302°F (150°C) (over a period of 2 years) respectively were identified to result in HTHA. Their study was with internally pressurised seamless tubes with 1 inch thick walls.

A number of interesting observations are made on studies investigating the effect of steel making. These include the effect of hydrogen purging during steel-making to remove impurities that would otherwise later react with hydrogen, and the beneficial effect of carbide stabilisers such as Chromium. Furthermore, parallels are drawn between HTHA in copper where unstable oxides rather than carbides are attacked which leads to the suspicion of similar unstable compounds/non-metallic impurities (with elements O, N, S, P) being affected in the HTHA of steel. Steels ‘killed’ (de-oxidised) with aluminium are claimed to be more resistant to HTHA than non-killed steels due to the greater stability of the Al2O3 compared with Fe3O4 that would otherwise form. A ‘sorbitic’ heat treatment is advised because it finely distributes pearlite and avoids grain boundary carbides, which are deemed to be more harmful.

The effects of stress and cold work are considered as accelerating factors linked to increased diffusion and solubility of hydrogen in the steel.

The effects of chemical accelerators and inhibitors are also discussed in the context of hydrogen absorption into the steel. For example, reference is made to an experiment where hydrogen diffusion through a piece steel at 392°F (200°C) was greatly enhanced by a coating of NaSiO4 but inhibited by a coating of Na2CrO4. No mention of the effect of welds is made.

5.1.2 Point 16 – Evans 1948

This paper describes the results of investigations of process equipment operating at 437 - 698°F (225 - 370°C), 350psi (24bar) with service lives between 0.5-6 years, made from carbon steel plate and pipe with various welding configurations (no mention of PWHT condition). Out of 29 investigations, 12 were identified as having hydrogen attack after two or more years of operation. Bend tests and metallographic techniques were used to identify hydrogen attack. It is shown that different steels within the same component suffered from different degrees of attack and concludes that 0.10-0.35% carbon steels are susceptible to HTHA at 572°F (300°C) and 350psi (24bar) and that the time and location at which attack could occur cannot be predicted accurately. There are numerous results shown above these guideline values that did not suffer attack, demonstrating the unpredictable nature of the phenomenon. The only result taken from the investigations used in the Nelson curve diagram is that of a no-attack result at conditions of 437°F (225°C), 2 years.

5.1.3 Point 19 – Ciuffreda and Rowland, 1957

This involved three reactor vessels of a fixed bed catalytic reformer (Powerformer) operated by Esso Standard Oil Company’s refinery in Baltimore, Maryland, in 1956 after one year of operation. They operated with a naptha-hydrogen vapour mixture at approximately 955°F (523°C), 330psi (23bar). The vessels were constructed with 1 5/8” silicon killed carbon steel (ASTM A201-Gr.B), composition shown in Table 4 and the design targeted a shell temperature of 300°F (149°C) in recognition of HTHA and the carbon steel Nelson curve, published in 1955 (Nelson, 1955), which is essentially in the same place as the 2016 edition. However, within
one month of start-up, it was identified that the average measured shell temperature was between 600 and 750°F (315 - 402°C).

It is not entirely clear from the paper whether there was some shrouding missing from the fabrication that was present in the design that would have helped to control temperature. In any case it was decided to run the vessel and order shrouding for installation and carefully monitor temperatures in the meantime. External shell temperatures were measured at numerous locations on the vessel wall OD and a good understanding of the vessel temperature was built up prior to failure. It was not considered particularly risky to proceed in this manner as other units operated at Baltimore were known to have operated at high pressures and temperatures (800°F (427°C), 230psi (16bar) and 710°F (377°C), 450psi (31bar)) for approximately 2 years.

Two vessels failed due to the appearance of large through wall cracks totalling 63 and 125” (1600- 3175mm) in length, and the third vessel failed a post-incident pressure test at 150% design pressure and so was also included in further investigations. Cracking was found to have initiated at the toe of a poorly finished weld, i.e. a stress concentration, and not in the areas where the most severe attack was identified in the microstructures. The conditions corresponding to the failure position were 330psi (10.5bar), and an ‘average’ temperature of 740°F (393°C).

Further metallurgical investigations carried out involved 180° bend tests, at room (ambient) temperature, from different areas of each the vessels and mapping the results against the relevant average temperatures. No cracking during bend test was considered as a pass. An average OD wall temperature below which the bend test passed was thus identified. The lowest value corresponds closely to the relevant point plotted on the Nelson curve, i.e. 330psi (23bar), 575°F (302°C), some 40°F above the curve. All “average” temperatures reported were above the numerical mean average for the location of interest, in recognition that higher temperatures were likely to cause damage more quickly, but it is not clear how this was calculated. The mean temperature would have been closer to the curve, but it is not clear by how much. Metallography showed complete though wall decarburisation and fissuring up to 0.75” in the hottest areas. It is highlighted that light microscopy could not necessarily identify when a bend test would pass or fail indicating a transition period before the microstructure obviously breaks down. It was also highlighted that decarburisation could take place sub-surface and was attributed to compositional differences in different regions.

The paper identifies the importance of stress effects and time for HTHA to take effect. The discussion section includes a comment by Nelson that this information will be used to supplement the data in the diagrams, but that the Nelson curve should not be lowered as a result. Although it is possible that these data should have been given more weight owing to uncertainties over the ‘average temperature’ determination and the means of detection of HTHA, the study is relatively detailed and convincing.

5.1.4 Point 26 – Moore and Bird, 1965

This paper describes corrosion issues with a hydrogen plant that produces near pure hydrogen from natural gas and steam heated over a catalyst, with CO, CO₂ and H₂ being the products and excess CO and CO₂ being stripped out of the effluent. There is a small section describing a failure of a carbon steel installed instead of the specified 1.25CrMo steel tube. Conditions were estimated as “probably” 700°F (371°C), 220psi (104bar). This point is relatively far away from the carbon steel Nelson curves.

5.1.5 Further observations by other authors on the API RP 941 data

The API TR 941 (Technical Report) produced before the Tesoro incident identifies 22 pieces of correspondence that are in “the file” but not plotted (API, 2008b). Seven of these refer to carbon steel and have durations and service conditions associated with them and one is within the 700°F (371°C), 700psi (48.5bar) range of immediate interest and is plotted in Figure 6.
Interestingly, this point (at 497°F (258°C) 650psi (45bar)) represents a failure and is situated 20°F below the primary carbon steel Nelson curve and therefore represents a concerning piece of data that may not be well represented by the existing Nelson curve. The point is reportedly associated with ‘high stress areas’. That data point along with the others pertaining to carbon steels are listed in Table 5. It is not always clear whether welds were involved.

5.1.6 Further notes on the carbon steel curve data

An analogous plot due to Shuyten (1947), produced prior to Nelson’s curves is presented in the technical report API TR 941 (API, 2008d) featuring a limit line for parent carbon steel that falls to below 400°F (204°C) at pressures beyond 2400psi (165bar). This is in line with the work referenced in the diagram by Inglis and Andrews, 1933 that revealed damage in laboratory experiments at 302-347°F (150-175°C), 3674psi (253bar) with a hoop stress of 54MPa after 17,600 hours (2 years). Their study also showed that a fine grain heat treatment could markedly improve the resistance of the same steel to HTHA. Although these pressures are outside of the immediate range of concern, the points do fall below the current curve for carbon steel. The relevant data are presented in Tables 4 and 6.

Silfies et al, 2016, appear to have had access to relevant API files and confidential Materials Property Council data and have been able to find some additional details including some more details about the durations. Unfortunately, they did not specifically link duration to service conditions in their paper. However, Nugent et al, 2017 did reveal six durations for the data points in the range of interest that are not provided in the standard. These durations are provided in Table 3.

The Nelson curves for carbon steel are based on both industry experience and experimental data points. Although the information concerning the data, especially for the service data, is not very thorough, there is a degree of inherent margin within them as the operating conditions and exact metallurgical state are various and imprecise, meaning that they encompass a distribution of material and operating conditions, at least some of which will have been conservatively estimated. Nelson is reported to have included a safety factor in his original plots of approximately 30°F (API, 2008). The carbon steel curve in particular is considered to have served the industry very well since its conception up until recent events (API, 2008c)(CSB, 2014b), which all seem to be associated with non-PWHT’d welds. This is in contrast to the 0.5Mo curve that was found to be unreliable soon after the first issue of API RP 941. It should also be noted that it is reasonably common for refinery engineers to apply an additional safety factor to the curve for design purposes of between 25-50°F and 50psig (API, 2008)(MTI, 2016)(McLaughlin et al. 2010). Note that the Tesoro procedures would have triggered an HTHA inspection if conditions were identified to be within 25°F of the Nelson curve. Therefore if temperature had actually been measured or even calculated for the heat exchangers, an inspection may have been triggered, potentially preventing the failure from occurring.

There is clearly a time element that is not accounted for sufficiently in API 941, which is influenced by other factors such as the steel condition (stress, cold work composition and heat treatment) and also by the details of the environment (fluid mixture composition, surface reactions, contaminants, temperature and pressure). Essentially, there are very few data points with service lives in the region of those failures experienced recently that can be used to validate the curve placement for similar durations. A histogram showing the durations of data points, where available, from the API standard and the technical report is shown in Figure 7. Unless it can be proved that there is a fundamental limiting temperature and pressure for HTHA to take place for a certain steel then, there will always remain some uncertainty over continued performance over longer durations and therefore the inspection regulations should be adjusted to account for this.

5.2 The non-PWHT’d carbon steel Nelson curve in Figure F.1 Annex F

The 2016 edition of API RP 941 features an annex that recognises a number of HTHA incidences occurring since the year 2000, in which non-PWHT welds were compromised. Eight
points relating to these instances are shown in Figure 6. A new Nelson curve for this material condition has been provided in the standard that approaches 450°F (232°C) at 700psi (48.5bar). Each data point has a duration associated with it and some degree of detail given in the comments section of the same Appendix. Durations range from 4.5 to ‘30+’ years. The conditions for the Tesoro incident are not apparently represented in the diagram.

All the points are referenced as private communications bar one, Point 34, which has a reference in the literature: McLaughlin, 2010.

5.2.1 Point 34 - McLaughlin, 2010

This describes an investigation into the cracking of welds in a reactor vessel and associated heat exchanger sections of a hydrotreating unit built in the late 70’s from ASTM A-515 grade 70. A period of three years was identified when the unit was operated at higher pressure and temperature (550-600°F (288-316°C), 100-200psia (7-14bara) including several excursions beyond the carbon steel Nelson curve. Four years after this period, a leak due to through wall cracking was identified.

McLaughlin reasons that HTHA took place during the three year period where more extreme conditions were identified resulting in “Stage 1 cracking” by HTHA. Although the crack tips shown in some of the figures presented in the paper do appear to have a degree of intergranular character, the appearance is not immediately identifiable as HTHA damage as there is very little incipient cracking or de-carburisation identified. McLaughlin claims that ‘...the cementite (Fe3C) carbide has experienced some degradation...’ and that ‘...the fissures shown ... suggests that Stage 1 cracking is not associated with the same time dependent creep mechanism generally associated with HTHA.’ The evidence provided does not readily support these assertions. The final stage of cracking “Stage 2” is blamed on sulphide scale packing the existing crack and acting as a wedge, exacerbating thermally induced stresses at the crack tips during shutdowns. This is reasoned to contribute to a relatively small proportion of the crack length with only two shutdown events identified where such cracking could have taken place during the four-year period between Stage 1 and failure.

Considering the unit did operate above the carbon steel Nelson curve (for non-welded or welded with PWHT) on occasion and that this period of operation was associated with the HTHA damage it seems somewhat unfair to place this point below the existing Nelson curve. Furthermore, the presentation of the metallurgical results in the paper are not thoroughly reported and so it is difficult to make confident judgements on the character of the cracking experienced and be convinced of the presence of HTHA at all.

An inconsistency seems to exist between the API Standard and the paper regarding duration. McLaughlin asserted that the majority of cracking took place over a period of three years, whereas the comments section of the standard states a service period of ‘30+ years’. The temperature and pressure value represented by the associated Point 34 in Annex F of the standard seems likely to be an average value from the three-year period.

5.3 Figure 3 - Incubation time for carbon steel

Figure 3 of the standard shows estimated incubation time for HTHA to get to a detectable stage. It consists of several isochrones from 100-10,000 hours on a plot of temperature and pressure with the Nelson curve from Figure 1 being represented as no attack (effectively infinite time). This is described in the standard as useful for determining whether an excursion above the Nelson curve poses a risk of HTHA in the period of concern. It also brings to light that HTHA is very much time dependent and that the kinetics, i.e. the rate of the methane reaction, depends principally on the temperature and hydrogen pressure.

No direct references for the curves are given in the 2016 version of the standard. However earlier versions reference Nelson, 1965 directly. The 2016 edition also lacks clear referencing of the individual data points and earlier versions are more useful in this regard. There are 12
references for the 29 data points shown. Seven references are in common with those of Figure 1 of the standard and five references are unique to data points in Figure 3 of the standard. The data points and their references are presented in Table 7 and Figure 8. Figure 9 is a histogram showing the frequency distribution in terms of duration associated with the data. It is clear that the vast majority of the data (>95%) have durations of less than four years.

Nelson, 1965 (Earliest publication of the incubation plots), indicates that both points with and without attack are plotted in the figure. Precise incubation times are given where possible (from experiments) otherwise the time prior to discovery was indicated (for data relating to field service). Where no attack was found then a duration greater than that relevant to discovery was indicated providing a conservative value. The data are therefore not all incubation times derived from experiments but are a mixture of observations from industry and incubation times calculated from detailed experiments. The methodology used to construct the curves is not explained, but it is presumed that the line for no attack has been translated to higher pressures and temperatures to represent smaller incubation durations.

The incubation figure is a useful tool for prediction of the first appearance of hydrogen attack. However, what it does not account for is the time that it may take for attack to progress through a thick walled vessel, to a stage that will compromise the integrity. This is discussed further in Section 7.1.1.
Parametric models with pressure, temperature and time

Weiner, 1961 appears to have made the first attempt at predicting incubation times based on relationships determined from experiments. Incubation times were taken as the time taken for the ductility of miniature specimens (0.09"/2.3mm) to begin to degrade. A number of experiments at temperatures between 800-1100°F (427-593°C) and 450-950psi (232-510bar) were performed. An Arrhenius relationship to the temperature and a power law for the pressure dependence were combined into one equation:

\[ t_0 = CP^{-n}e^{Q/RT} \]

Where C (constant) = 1.39x10^6, n (constant) = 3 and Q (activation energy) = 14,600 cal/mole, P = Pressure, R = Gas constant.

Allen et al, 1961, 1962 carried out a similar analysis using the time for 50% attack for SAE grade 1020 and Ferrovac 1020 steel specimens 1/16"inch (1.6mm) exposed at temperatures and pressures of 700-1000°F (371-538°C) and 400-1400psi (27.5-96.5bar). They obtained the following constants:

C = 4.11x10^3, n = 2 and Q = 15,200 cal/mole

Vitovec, 1977 used the data from the Nelson curve (Nelson, 1965) in a similar way, deriving a similar relationship but providing different Q values for low temperatures (<310°C = 590°F).:

\[ t = C.T^{-1}.P^{-n}.e^{Q/RT} \]

Parent >310°C: C=4.5x10^{12}, n=3.6, Q=7,500 cal/mole
Parent <310°C: C=7.117x10^{-61}, n=3.6, Q=21,000 cal/mole

Panda and Shewmon, 1984 have performed dilatometry experiments in hot hydrogen and measured the expansion rate due to the expansion of cavities or methane bubbles. From this a strain rate could be determined for a sample length and related to a bubble density and size. Effective activation energies have been determined from the plots related to the strain rate \((d\varepsilon/dt)\) against 1/T and the following expression arrived at:

\[ d\varepsilon/dt = CP^n.exp(-Q/RT) \]

if this is integrated with respect to time t:

\[ \varepsilon = CP^n.exp(-Q/RT).t \]

This expression has been manipulated by the Japanese Pressure Vessel and Research Council (JPVRC), to create a parameter known as \(P_w\), API,2008e.

Taking logs and rearranging:

\[ \ln C - \ln \varepsilon = -n\ln P - \ln t + Q/RT \]

where \(P_w = \ln C - \ln \varepsilon\)

This has been used as a way of estimating incubation time. This was achieved by determining \(P_w\) at \(t=100,000\), \(P = 1000psi (69bar)\) and \(T = 500°F (260°C)\) (sitting on the ‘no attack’ line for carbon steel in API RP 941) and \(n = 0.375\), \(Q = 190kJ/mol\).

Once a \(P_w\) value of 30.63 has been determined from this calibration, other incubation curves can be calculated.
These three expressions have been used to plot 10,000-hour lines on the API RP 941 incubation curves, as shown in Figure 10. It is clear that the parameters are limited in their agreement with each other and with the incubation curves. Using limited data created at temperatures and pressures far outside typical operating ranges is not ideal, and any parameter that uses the existing Nelson curve to calibrate on is only as good as the Nelson curve.
Definition of the HTHA mechanism

The problem of HTHA has been recognised as early as 1908, when Bosch and Haber had trouble with their reaction vessels used for the synthetic production of ammonia by direct combination of nitrogen and hydrogen at high temperatures and pressures (Fletcher and Elsea, 1964). It was thus established that exposure of materials to hydrogen gas at elevated pressures and temperatures can result in a form of material degradation that is referred to as HTHA. The Nelson curve is the most common expression of the temperatures and pressures of concern.

Practically, a fall in the mechanical properties and carbon content can be measured, and changes in the microstructure can be observed (Weiner, 1961; Victovec, 1982) (Figure 11). Micro-fissures along grain boundaries and local decarburisation are defining metallographic features of the phenomenon. Decarburisation and development of fissures is mainly associated with the generation of an internal methane pressure due to the reaction of hydrogen with carbon at favourable reaction sites. The reaction therefore relies on the diffusion of hydrogen into the steel and free carbon from the steel. The methane molecules cannot dissolve or diffuse and so a methane pressure develops at the reaction interfaces, which may be pre-existing micro-voids or grain boundaries, causing internal stresses. In typical carbon steel, the nucleation of methane bubbles at pearlite grain boundaries is commonly implicated. Evidence of such bubbles has been presented by way of high magnification SEM images. The development of such bubbles has the additional requirement of mass movement of the steel, meaning the deformation or diffusion of material at the bubble interface involved with their creation. Fissuring of the steel aligned with the reaction sites occurs once a critical methane pressure has developed. At high temperatures, and low pressures, surface de-carburisation due to the methane reaction dominates and internal fissuring is less of an issue.

7.1 Stages of attack

The development of HTHA can be thought of as taking place over a number of stages. Vitovec, 1964 described a five stage process presented in Table 8. More recently, four stages have been described by Vitovec 1982 and in API RP 941:2016. These are presented side by side in Table 9. As can be seen, the API description focusses more on the actual measurable identifiers, whereas Vitovec’s is focused on the mechanisms at work. A plot of various measurable attributes helps illustrate the development of attack as shown in Figure 11. Measurable attributes include yield strength, UTS, reduction of area, Charpy impact, bend angle (before fracture), volume increase and specific gravity. Note that some attributes are more sensitive than others are. Such plots made by Weiner, 1961 and Vitovec, 1964 show that the incubation period (Stage 1) can vary dramatically depending on temperature and pressure while the rate of change (slope of the line) for Stage 3 is similar for a variety of pressures and temperatures. The incubation time is therefore the stage that varies most and is of principle concern when considering how to improve resistance or predict service lifetimes.

7.1.1 Through wall progression of HTHA

It is worth mentioning that the above stages have been defined using small scale experiments, where hydrogen exposure was from all sides, and the volume of material was very small relative to a pressure vessel wall or pipe thickness. In a real pressure vessel, attack tends to progress through wall so there is a gradient of attack from the surface in contact to the outer surface. The dissolved hydrogen and temperature gradient through wall will play a significant role in the thick wall vessels, explaining why the attack progresses in such a manner. This means that the internal surface of a pipe may be in Stage 4 (according to the descriptions above), while the external surface is at Stage 1.

An example of how HTHA damage may progress through the wall of pressure vessel parent plate due to HTHA is presented by Lundin et al, 2014, for C-1/2Mo steel. This involved the study of a retired heat exchanger channel that had seen 28 years of service with the maximum temperature and pressure estimated as 580°F (304°C) and 950psi (65.5bar) respectively.
Specimens were extracted at various positions through wall to measure the variation in mechanical properties as well as to assess the metallographic evidence of damage and the amount of CH₄ retained in the steel. The damage was seen to progress from the ID, where the steel surface is exposed to the process fluid. The change in measured values through the wall were plotted and a schematic representation of them is shown in Figure 12. As can be deduced from the Figure, the reduction in CH₄ concentration and microstructural damage corresponds to an increase in the properties through wall. This would also correspond to the through wall dissolved hydrogen concentration and temperature gradient that would exist in service. In this particular case, lamellar fissuring in the rolling plane was located at the ID where most of the damage had occurred. The observations and measurements made in the study provide evidence that HTHA typically progresses through wall over time and therefore a gradient of damage will exist. Generally, the progression of damage through the wall is expected to occur in this way and that eventually micro-fissures join up or concentrate into more prominent flaws that lead to a fracture in the vessel wall. However, if there are sharp flaws present and or non-PWHT welds, this effect appears to be greatly accelerated in the region of such features. It is therefore vital to understand the distribution of flaws, welds and stresses when estimating the remaining life of a vessel.
Crack Propagation in HTHA conditions

As indicated in the previous Section, cracks may develop over time due to HTHA. Understanding the behaviour of such cracks can be useful in predicting safe operating service lives for equipment. However, understanding crack propagation in HTHA conditions is challenging, making fracture based assessments more difficult.

For ‘classical’ or conventional fracture toughness testing in air, specimens are typically subjected to a continuous rising load to determine their resistance to fast fracture - brittle and/or ductile tearing. The data generated is used to determine the critical crack tip stress intensity that the structure can sustain at a given moment, i.e. the ‘critical toughness’.

In the presence of hydrogen at room temperature, slow, hydrogen assisted crack propagation can occur at crack tip stress intensities far below those determined by classical critical toughness tests in-air. This is also the case in hot hydrogen, for which propagation will be dominated by HTHA mechanisms. Under these circumstances, diffusion and creep processes play a significant role and cracks can slowly grow until they reach a critical size (defined by conventional fracture toughness tests).

Thus to perform a fracture assessment, the following data is of importance:

- Hydrogen assisted crack growth rate as a function of crack tip stress intensity for the temperatures and hydrogen pressures of concern.
- Critical toughness, i.e. that governing the final fracture.

Previous studies of crack propagation associated with HTHA have used a fixed displacement wedge opening load methodology (Shewmon and Xue, 1991; Chen and Shewmon, 1995) and have shown that flaws can progress via HTHA at the grain boundaries and that the temperature and hydrogen pressure greatly affect the crack growth rate. Significantly, this crack progression can occur even when there is no detectable damage in material volume remote from the crack front and could nucleate form pre-existing flaws prior to any gross HTHA damage.

Whether crack propagation is slow sub-critical growth during service or fast fracture during failure, it should be recognised that progression will be through material with various degrees of HTHA damage and that dissolved hydrogen concentration, temperature, pressure, and stress variations. Additional complications arise when certain microstructures are of interest, such as for welds.

It has been shown that the critical toughness is likely to be affected by the level of pre-existing HTHA damage present in the material through which the crack will propagate during final failure (Wilkowski et al, 2018). The influence of hydrogen on final failure (i.e. fast crack propagation) is a subject of on-going research, but is expected to have a secondary effect based on TWI experience with room temperature tests. Ideally, fracture assessments should also consider start-up and shutdown conditions for which temperature gradients can cause large thermal stresses.

It is clear that obtaining accurate data is challenging and that this in turn can reduce the confidence in any fracture assessment procedure. There is currently no guidance in standards on the measurement of fracture toughness in hot hydrogen environments. Nevertheless, if the limitations of the testing and assessment methods are well understood and explained, then a reasoned assessment can be made. Industry are currently exploring fracture assessment approaches for HTHA damaged equipment, and it is known that an API 579 task group has been formed to aid the introduction of specific guidance on fitness for service assessments for HTHA (Exxon, 2017). However, fracture toughness testing associated with HTHA, and predicting the development of HTHA damage remain the subject of on-going research.
8.1 Leak-before-break considerations

Flaws that provide a leak path in pressure equipment are typically classed as unacceptable, but there are circumstances where a leak-before-break assessment can be appropriate.

Leak-before-break situations are those where a stable leak in a pressure boundary develops rather than a sudden loss of pressure containment. Under conditions where the environment has a known and quantifiable effect on material properties, fracture mechanics assessments are employed to determine whether leak before break is viable, using the relevant fracture toughness data and the specific geometry and operating conditions. BS 7910:2015 and API 579-1:2016, among others, describe methodologies for assessment of pressure vessels and piping. However, major challenges exist to understand the way in which a pre-existing flaw will develop and to obtain accurate fracture toughness properties for materials under HTHA conditions, as highlighted in the previous section. One of the primary concerns with regard to flaw development is the gradation in material damage through wall, which will be pertinent to crack growth rate and hence to the development of crack front shape. Furthermore, there would need to be confidence in the dimensions of the flaw to be assessed in the leak before break assessment. The situation is further complicated by the known difficulties in the detection of HTHA damage. The sometimes diffuse and highly branched nature of HTHA make it particularly challenging to predict crack development. However, where cracking is concentrated, for example in a weld HAZ, it may be easier to treat the damaged area as an idealised flaw.

It should also be recognised that during start-up and shutdown, there may be material with a high concentration of dissolved hydrogen and low metal temperature that needs careful consideration in terms of brittle behaviour.

The Tesoro incident does not appear to be a leak-before-break situation, as no through wall cracking or leaking from the vessel itself was identified (Note the reported history of leaking in the CSB report is associated with the heat exchanger flanges). A posthumous fracture assessment of the vessel could be of some interest to identify what the expectation would have been, given the flaws present in the exemplar Exchanger B. There are several examples of leak situations identified in API RP 941 and the accompanying literature, e.g. McLaughlin, 2010. It is not known to the author whether any such leak-before-break assessment was carried out in any of these cases.
9 Chemical aspects

The development of attack is fundamentally controlled by the synthesis of methane from carbon and hydrogen:

\[ C + 2H_2 = CH_4 \]

However, there are many chemical processes and complications involved that make it difficult to determine the thermodynamic viability and the kinetics of the reaction.

First, H\(_2\) has to dissociate and dissolve in the steel. The solubility will change with temperature, pressure, stress and metallurgical factors. Hydrogen will diffuse interstitially through the steel described by a diffusion coefficient. Such coefficients have been found to vary enormously even under careful laboratory controlled environments. A concentration gradient of hydrogen will exist from the exposed surface to the non-exposed surface and will be present in diffusible or trapped states influenced by the strain and specific microstructure and composition. The proportions of which are likely to have an influence on chemical potential of the reaction and the rate.

The availability or activity of carbon for reaction will be determined by the composition and heat treatment. A quenched steel contains excess carbon in solution, whereas in a tempered steel, the carbon is present as a carbide (typically \(M_2C\) for carbon steels) with an adjacent dissolved atmosphere of diffused carbon in equilibrium with the carbide. Carbon diffusion to reaction sites will result in the dissolution of carbides as the methane reaction proceeds. The rate of dissolution will be affected by the size, shape and composition of the carbides. If the carbide is in direct contact with the reaction site and the hydrogen then a more direct reaction can take place.

The reaction sites are higher energy parts of the microstructure where the C and H in solution can combine. The exact nature of these sites is not clear in the first instance. Most theories are to do with “sub-microscopic voids” or “micro-cavities”, where hydrogen is present in diatomic form at the same pressure as that applied externally.

Shih, 1978, considered the thermodynamics of the reaction:

\[ Fe_3C + 2H_2 = 3Fe + CH_4 \]

A Gibbs free energy (\(\Delta G\)), i.e. the total energy which is released by a reaction indicating the thermodynamic viability of a reaction occurring, was calculated indirectly by the summation of values available in the literature for the dissolution of carbon from the carbide in ferrite:

\[ \Delta G_{Fe_3C} = C_{(sol)} + 3Fe \]

and for the formation of CH\(_4\) from diatomic hydrogen and dissolved carbon

\[ \Delta G_{C + 2H_2} = CH_4 \]

Shih determined that \(\Delta G\) increased linearly with temperature to zero at 1045°F (563°C), meaning that the reaction is only thermodynamically feasible below this temperature. (Note: this is well above the safe limit for operation of carbon steel)

Using the expression:

\[ \Delta G = -RT\ln K \]

An equilibrium constant could be determined for
\[ K = \frac{f_{\text{CH}_4}}{f_{\text{H}_2^2}} \]

Where \( f_x \) is the fugacity. By assuming \( f_{\text{H}_2^2} \) in the voids is the same as the applied pressure, a value for \( f_{\text{CH}_4^2} \) was estimated at 600°K (440°F or 227°C) indicating an equilibrium methane fugacity of \( 1.3 \times 10^7 \) atm, i.e. many times higher than the hydrogen pressure and the breaking stress of steel.
10 Influence of material factors

10.1 Alloying additions

Carbon is the necessary ingredient for methane formation, and the amount of carbon and its form can make a difference to the rate of attack (Shewmon 1976; Sundarajan & Shewmon 1981; Shewmon 1985; Parthasarathy 1985; Lopez 1987). Carbon activity increases with carbon content of the steel, but can be effected by heat treatment and carbide forming elements, API TR 2008. Weiner, 1961 showed that high purity iron with carbon < 0.004wt% was not attacked whatsoever at 1000°F (538°C); 700psi (48.5bar); 500hours. Another study by Allen et al. (1961) showed that a high purity steel with a 90ppm carbon content was attacked more slowly at a relatively low temperature (700°F (371°C), but that at 1000°F (538°C) the time for attack was significantly accelerated compared to the commercial steel SAE1020, containing 0.23% carbon.

Weiner, 1961 also showed that for a steel with 0.12wt% C, a spheroidising treatment that coarsened the carbides increased the incubation time five-fold. Furthermore, Shewmon & Xue (1991) found a spheroidised structure more resistant to crack growth than a normalised structure. Prescott (1983) however suggests a spheroidised structure is likely to have a low resistance to HTHA. In any case spheroidising, is itself considered a degradation mechanism and not ideal from a mechanical properties perspective. Parthasarathy and Shewmon, 1984 showed the effect of tempering parameter on the carbon activity and the much reduced rate of attack associated with low activity, for a 2.25Cr 0.5Mo steel.

Strong carbide formers can lower the carbon activity and improve the HTHA resistance. Naumann, 1938 ranked them in the following order (high to low): Ti, V, Zr, Nb, Mo, W, Cr and Mn; Si, Ni and Cu not providing any beneficial effect. A carbon steel that has traces of these strong carbide formers is likely to have marginally increased resistance to HTHA. Cr and Mo are the main elements used in low alloy steels to improve HTHA resistance among other properties. Additions of Cr above 3% have a marked effect on performance.

10.2 De-oxidising practice and impurities

Weiner, 1961 identified that the addition of an Al de-oxidising agent to steel with very low S and P, halved (worsened) the incubation time and reasoned that reaction with oxides to form steam was inhibiting (preventing) the formation of CH₄ in the first instance. On the other hand Pishko et al 1979, found that Al used as a de-oxidising agent roughly doubled the performance compared to commercially available de-oxidising practises and therefore could be considered the most appropriate commercial treatment. The tentative conclusion to be drawn from this is that de-oxidation could actually have a negative effect, but as it is necessary for other reasons, then the most favourable way of achieving it is with Al treatment.

In the case that methane forms at voids/inclusions in the steel, then the nature of oxides, MnS and other inclusions are likely to play a role in providing nucleation sites. Surprisingly, Allen et al, 1962, found that cleaner steels (with fewer inclusions) were attacked more rapidly. This could be because pre-existing voids (essentially inclusions) of this type have relatively large volumes and may be able to accommodate more CH₄ in the first instance, without the adjacent material taking up the strain. This may have some relevance in the weld metals of higher alloyed materials where carbon activity is lower. However, in real service scenarios, where stresses are present, then inclusions tend to reduce the toughness of the steel which can help to enhance crack nucleation and propagation. The tentative conclusion is that steels with fewer inclusions may demonstrate shorter HTHA incubation times, all other things being equal.
10.3 Heat treatment and microstructure

The effect of tempering to form carbides and reduce the free carbon available for reactions has been touched upon above. Carbon steels are supplied in a number of different conditions – normalised, quenched and tempered (QT) or thermo-mechanically controlled processed (TMCP). There is very little literature investigating the effect of different heat treatments on HTHA available. However, treatments that offer refined grain sizes and well tempered carbides are likely to be the best. Commercially this means that normalised steels would offer a good compromise. TMCP steels can have very fine grain sizes and low carbon contents but may be rapidly cooled and are not tempered. Low strength plain carbon steels are not usually QT. However, there is no systematic study of the effect of steel heat treatment on HTHA resistance in the literature.

Weiner, 1961 found the incubation time roughly doubled for a grain size of ASTM 7.5 versus ASTM 5. Inglis and Andrews, 1933 showed that a fine grain heat treatment could markedly improve the resistance of the same steel to HTHA with at least a doubling of lifetime observed for the fine grain steel. They claimed that this could equate an increase of 50-100°C in service temperature.

At the incubation stage of attack it appears that a heat treatment can be given to restore the material properties. Weiner, 1961 heated some HTHA damaged specimens to temperatures between 1250-1650°F (680-899°C) and found that the yield and ductility could be almost fully restored despite the persistence of voids (albeit more isolated compared to a continuous network at the start point). It was hypothesised that CH₄ is broken down and that C dissolves in the steel which is consistent with the observed re-appearance of a yield point.

10.4 The significance of welds

Several studies have shown that welds and particularly the HAZ are more susceptible to HTHA than the parent metal, possibly due to higher levels of carbon activity in the HAZ (API, 2008). Sakai & Kaji (1978) reported a HTHA bubble or void density in the HAZ orders of magnitude higher than in the base metal. While others have found no difference between HAZ, weld and base metal (Erwin, 1981). Chen & Shewmon (1995) found crack growth rates in the HAZ under HTHA conditions were substantially faster than the base metal for 2.25Cr-1Mo steel.

Dilatometry has been used to compare the constant strain rate between base metal and welds (Parthasarathy & Shewmon 1987) which found that the HAZ swelled at twice the rate of base metal but less than the weld metal. This is contrary to others (Chao et al 1988, Prager, 1997, Bocquet et al 2000, Balladon et al 2003, Manna et al 2007) who have found the HAZ to be the most susceptible to HTHA and to industrial failures in the HAZ (CSB, 2014).

The high susceptibility reported for HAZs is logical given the trends in contributory factors highlighted in this report. The grain coarsened HAZ is a region that has a relatively large grain size next to the fusion line due to the thermal cycle it has been subjected to. It has been rapidly heated and quenched from the austenite phase field, which means that carbon has very little time to form precipitates resulting in increased C in solution and a higher carbon activity. If no PWHT is given, then the carbides will not develop and the C activity will remain high. Furthermore, weld residual stresses provide a driving force for the development of voids, or cracks and flaws introduced by the welding process. In conclusion, there are several factors that suggest that welds should be more susceptible compared to the base metal.
11 Influence of temperature and hydrogen pressure

The Nelson diagram illustrates the influence of temperature and pressure. Notably, the influence of pressure is large between 0 and 500psi (34.5bar) and then becomes relatively insignificant per unit increase, whereas, the temperature effect is notable beyond 100Psi. At high temperatures (>550°F (288°C) and low pressures (<200psi (14bar)) surface decarburisation and the activation of other mechanisms such as creep may become more prominent. The effect of excursion above the Nelson curve can be assessed by using the incubation curves and should be treated as additive, i.e. damage will accrue at a faster rate during the excursion and reduce the lifetime proportionately.

11.1 Partial pressure of other hydrogenous gases

Two additional gasses often of interest in process streams are CH₄ and H₂S. Vanick, 1927 carried out some of the earliest work with H₂, NH₄, N₂ mixtures and a wealth of work followed with similar mixtures (See Fletcher and Elsea, 1964). Vanick, indicated that the reaction of ammonia with the steel surface can liberate hydrogen and therefore provide additional hydrogen concentration for attack and thus more highly alloyed steels are required in ammonia service. Alloyed steels can also form hard nitride layers that may cause other problems.

Iron sulphide (FeS) scale has been implicated as an aggravating factor, with failures in hot hydrogen service, due to wedge opening effects (McLaughlin, 2010). However, a detailed study by Elizer and Nelson, 1979, showed that attack of carbon steel was very much diminished where FeS corrosion product had formed in a 90%H₂ 10%H₂S mixture. It was suggested that the scale acted as a barrier to hydrogen entry.

The effect of other classic poisons that enhance hydrogen absorption at room temperature in steel such as As and Se, Zapffe, 1944, is not known. Similarly, possible inhibitors have not been explored much in the context of HTHA.
12 Influence of stress

Most of the experimental work carried out to date has been on unstressed specimens to isolate the effects of applied stresses from the nucleation and growth of CH₄ filled voids and bubbles. The internal stresses developed by void growth will be additive to the applied stresses. Since carbon steel equipment is essentially designed using allowable stresses based on tensile stress at the operation service temperature for the steel, it does not take internal stresses due to void growth into account or the reduction in strength associated with decarburisation and fissuring. Applied stresses will aid the formation of voids and increase hydrogen solubility.

It has been shown that stress applied simultaneously with elevated temperature and hydrogen exposure greatly accelerates HTHA. Allen et al., 1965 carried out a series of creep tests with carbon steels in Argon (inert) and Hydrogen at 1000°F (538°C). A substantially reduced rupture time at a given stress was identified in hydrogen. The difference increased with the hydrogen pressure. Much effort has been put into determining creep curves for specific materials to produce master curves and understand the variance possible for a given grade for high temperature applications in general. This has not been the case under conditions of combined creep and HTHA, since designs essentially assume that neither creep nor HTHA will be active, by working below the Nelson curve. Producing some more creep data at temperatures and pressures below the Nelson curve could be of interest, however, and would ultimately give more reassuring values for an allowable stress. The effect of rupture stress on alloy steels has been studied in much more detail (MTI, 2016; Pillot, 2011).

Thermally induced stresses can be particularly high at mixers (where hot and cold streams meet) and between dissimilar metal welds or coatings where the thermal expansion coefficient of one material is higher than that of the other. The influence of cyclic stresses and fatigue is not well studied for HTHA, but it is highly likely that fatigue crack growth would be accelerated.

In welds, residual stresses are generated that would act in addition to the applied stresses of service. These can be of yield magnitude and will persist unless a PWHT is applied. PWHT will only partially reduce the stresses and so they will always be of some concern with regard to cracking mechanisms. This was shown to be the case in recent failures affecting non-PWHT’d welds as was discussed previously.

Gross plastic strain has been shown to greatly increase hydrogen solubility and reduce HTHA incubation time. Ransick & Shewmon, 1981 and Clugston et al., 1983, studied the effects of prior deformation and revealed enhanced attack with pre-strained samples. This could be relevant to any cold formed equipment such as pipe bends.
Practical steps for assessment of HTHA

Although not the main subject of this review, it is worth reflecting on findings of the review in the context of carrying out an assessment of plant equipment.

The recent failures and API RP 941 2016, highlight issues over HTHA of welds that have not been PWHT’d in particular, and the suitability of the Nelson curves. A new curve was duly introduced in to the new edition to account for non-PWHT’d material. Overall, this document is judged to represent the best guideline for operating equipment in high temperature, high pressure hydrogen, especially for carbon steels. The main point of concern lies with the relative lack of long-term (>100,000hrs) / approx. 12 years) data associated with the curves, although this has been somewhat improved with the non-PWHT’d data introduced.

Therefore, a review of equipment age and fabrication records should be undertaken, and in particular, PWHT records should be sought. The material grades and overlays should be checked against the design. If there are incomplete records or discrepancies this should be reflected in the care taken during inspections. For example, it would be good practice to assume no PWHT if there is no record of one being completed.

Secondly, the operating history in terms of operating temperatures and pressures should be reviewed. If there are pieces of equipment where there are no direct measurements of temperatures and pressures, direct monitoring of the equipment should be considered, at least for a typical operating cycle. Only when this is not possible should modelling of the temperatures be relied upon.

In the case that plant is found to be operating within 50°F, 50psi of the appropriate Nelson curves in the 2016 edition, then it is advisable to plan regular reviews of the operating conditions and to carry out inspections of these components including NDE methods. If there are any doubts over the manufacturing and operational records, this should be reflected in the scope of the inspections. Locations of high stress, whether due to residual stresses or thermal expansion, should be targeted. If hotspots can be identified then these should also be prioritised.

Beyond this a replacement schedule for the equipment needs to be seriously considered, including options for substituting a more resistant steel (according to the Nelson curves). What firm evidence is there that something will last 40 years, even if it is operating below the line? Remember that HTHA is complicated and susceptibility can vary a lot. Other failure mechanisms could also be playing a role in the eventual demise of the component and interactive effects can be very difficult to judge in the long run.
14 Conclusions

Recent reported failures that have been recognised in API RP 941: 2016 have all been associated with welds that did not receive a PWHT, in common with the Tesoro incident.

Welds increase the likelihood of HTHA occurring especially in the non-PWHT’d state, as the associated material suffers from increased carbon activity, stress and grain size (CGHAZ). All of these factors have been identified as posing increased risk of HTHA.

The current version of API RP 941 (8th edition, 2016) takes into account welds without PWHT, presenting a new limit curve for this case.

From the in-depth review of the CSB report on the Tesoro incident carried out, it is judged quite possible that the conditions at the rupture position did exceed the Nelson Curve limits and that if the true process conditions had been known, then more care would have been forthcoming to review and inspect the component. However, minor attack (possibly up to Stage 4, but only a very small volume at the wall surface) was also found in other weld locations operating at lower temperatures, indicating that the Nelson curves in earlier versions of API 941 (pre 2016 versions) were not entirely adequate.

After extensive review of the literature, it is judged that the API RP 941:2016 is currently the most reliable reference available to the industry for provision of a limit for carbon steel, especially if the commonly applied safety margin of 50°F, 50psi is respected. Reliable manufacturing records and service temperature and pressure records are key to identifying the risk to a component. However, an infinite lifetime cannot be guaranteed and operators should carefully weigh up the risks involved with operating plant beyond the design lifetimes and certainly beyond 20 years, as there is very little evidence presented in the literature demonstrating lifetimes of this order. Furthermore, recent failures have all been of components with service lives of >20years, further undermining the concept of infinite life.
Technical Recommendations

In terms of equipment design, the generation of strength and creep data in the relevant environments may provide more reliable allowable stress values and help designs to be more inherently resistant. Such tests could also be used for qualification purposes for individual heats of material destined for HTHA service. At present, there are very limited data of this sort available for carbon steels and the testing approaches are not standardised.

There is presently no systematic study of the effect of different steel types on HTHA. Therefore, a study comparing normalised, quenched and tempered (QT) and thermomechanically controlled processed (TMCP) steels, could be helpful for identifying the most susceptible carbon steels by grade type.

In terms of immediate practical steps that plant engineers can take to help judge the risk of HTHA in their components, the following points are suggested:

- Review equipment age and fabrication records. In particular, PWHT records should be sought.
- Review operating history in terms of operating temperatures and pressures. The use of direct monitoring should be considered for all equipment operating with hot (>400°F /204°C) hydrogen.
- Compare material and operational history with the limits set in the latest version of API RP 941.
- Adjust inspection regimes and frequencies according to the level of information available. E.g. if the operation falls within 50F, 50psi of the limit for that material, then increased inspection frequency and/or sophistication could be employed.

This review has concentrated on the reliability of the Nelson curves in API RP 941 in the context of the Tesoro incident and the main factors that can adversely affect carbon steel in HTHA environments. This review is complemented by a sister report on the non destructive methods for HTHA (Nageswaren, 2018). However, there are two further areas worthy of review that would complement the current reports:

1) Fitness for service assessment guidelines, fracture toughness and crack growth rate testing for HTHA scenarios.
2) Modelling of the HTHA phenomenon to bring out the differences between the results obtained by different models and highlight the extent of their shortcomings.

Such an exercise would provide an insight into the difficulties involved and the reliability of such approaches. Furthermore, it could naturally lead into more state of the art industry guidelines and the next generation of modelling software for fundamental prediction of HTHA and its progression through steel structures. It became increasingly clear during the process of writing the current review that these areas are of significant importance to industry.

Specifically concerning the Tesoro incident, a thorough examination of the modelling exercise used to predict temperatures and pressures would be re-assuring, since this is the crucial evidence used to condemn the Nelson curves in the CSB report. Furthermore, a reverse engineering exercise using the Tesoro material, to understand critical flaw size, could be used to help shape and validate any future assessment procedure. However, this would require the cooperation with the CSB and possibly other organisations involved with the failure.
16 Acknowledgements

The author gratefully acknowledges the input from industry representatives from ArcelorMittal, Ineos and ExxonMobil, who reviewed the draft report. The input from colleagues from TWI (Tyler London, Menno Hoekstra and Richard Pargeter) is also gratefully acknowledged.
References


Pillot S et al, 2011: ”Hydrogen and high temperature resistant v-modified 9Cr-1MO heavy plates devoted to new generation on high performance petrochemical reactors”. July 17-21, Proceedings of the ASME 2011 Pressure Vessels and Piping Division Conference, 2011, Baltimore, Maryland USA


Table 1 Values relating to Exchangers B and E provided by Tesoro process engineering for a DMHR carried out by Lloyd’s Register Capstone. (Taken form Figure 31 of CSB, 2014)

<table>
<thead>
<tr>
<th>Design data provided</th>
<th>Data provided for Lloyds Capstone Assessment</th>
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<td>Hydrogen partial pressure, psi</td>
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<td>pressure, psi</td>
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<td>405-504°F (207-262°C)</td>
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<td>350-500°F (177-260°C)</td>
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Table 2 Historical record of the number of data points in the Nelson curves

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<td>9</td>
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<tr>
<td>API RP 941 1970</td>
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<tr>
<td>Nelson, 1949*</td>
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<td>12</td>
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*Determined from plot presented in API TR 941, 2008 (Figure A-2) (original paper not available).
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<th>°F</th>
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<th>°C</th>
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<th>Affected region</th>
<th>HTHA</th>
<th>API Ref</th>
<th>API Notes</th>
<th>API Annex 8 notes</th>
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<td>398</td>
<td>574</td>
<td>27</td>
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<td>C.A. Zapffe, &quot;Boiler Embrittlement,&quot; Transactions of the ASME, Vol. 66, pp. 81–126, 1944</td>
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<td>294</td>
<td>?</td>
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<td>API Refinery Corrosion Committee Survey, 1957</td>
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<td>561</td>
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<td>294</td>
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<td>Amoco Oil Company, private communication to API Subcommittee on Corrosion, 1960</td>
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<td>279</td>
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<td>Gulf Oil Corporation, private communication to API Subcommittee on Corrosion, 1976</td>
<td>After 8 years, carbon steel cracked</td>
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<td>7</td>
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<td>700</td>
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<td>371</td>
<td>4*</td>
<td>WM and HAZ only</td>
<td>Air Products, Inc., private communication to API Subcommittee on Corrosion, March 1960</td>
<td>Damage was concentrated in the weld and heat-affected sections of A106 pipe. Base metal on either side of this zone was unaffected</td>
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<td>Air Products, Inc., private communication to API Subcommittee on Corrosion, March 1960</td>
<td>Damage was concentrated in the weld and heat-affected sections of A106 pipe. Base metal on either side of this zone was unaffected</td>
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<td>Hot bent section</td>
<td>Amoco Oil Company, private communication to API Subcommittee on Corrosion, 1960</td>
<td>After 11 years of service, damage was found in the hot bent section of A106 pipe. Unheated straight sections were not affected</td>
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<td>356</td>
<td>591</td>
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<td>311</td>
<td>2</td>
<td>Pipe and plate</td>
<td>T.C. Evans, “Hydrogen Attack on Carbon Steels,” Mechanical Engineering, Vol. 70, pp. 414–416, 1948</td>
<td>In a series of 29 steel samples, 12 were damaged, while 17 were not</td>
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<td>602</td>
<td>591</td>
<td>42</td>
<td>311</td>
<td>2*</td>
<td>?</td>
<td>Shell Oil Company, private communication to API Subcommittee on Corrosion</td>
<td>After 2 years exposure, five out of six pieces of carbon steel pipe were damaged. One piece of pipe was unaffected.</td>
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<td>Union Oil Company of California, private communication to API Subcommittee on Corrosion, 1980</td>
<td>After 18 years, carbon steel did not show HTHA</td>
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<td>683</td>
<td>6</td>
<td>362</td>
<td>6</td>
<td>Flange HAZ</td>
<td>Phillips 66 Company, private communication to API Subcommittee on Corrosion, 2012.</td>
<td>-</td>
<td>After 6 years, multiple non-PWHT’d carbon steel flanges cracked in the HAZs on the flange side of flange to pipe welds in a gasoline desulfurization unit. Operating at roughly 670 °F and at 85 psia.</td>
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<td>643</td>
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<td>340</td>
<td>0.7*</td>
<td>Parent 27%</td>
<td>Eight separate points (failures) 35a through 35h. Valero Energy Corporation, private communication to API Subcommittee</td>
<td>A section made of A106 pipe was found to be damaged to 27 % of its thickness after 5745 hours. Other pieces of pipe in the same line were unaffected.</td>
<td>Points 35a and 35h. These 2 points on the plot represent the range of 8 different failures. After 4.5 to 8 years, 7 different non-PWHT’d carbon steel flanges cracked in the HAZs on the flange side of a flange-to-pipe welds in gasoline hydrotreating service. One cracked on the pipe side of the pipe-to-flange weld. Operating at 645 °F (340 °C) and 57 psia to 94 psia (0.39 MPa to 0.65 MPa) hydrogen partial pressure.</td>
<td></td>
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<td>°C</td>
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<td>Affected region HTHA</td>
<td>API Ref</td>
<td>API Notes</td>
<td>API Annex 8 notes</td>
<td></td>
</tr>
<tr>
<td>-------</td>
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<td>------</td>
<td>----------------</td>
<td>----------------------</td>
<td>---------</td>
<td>------------</td>
<td>------------------</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>Non PWHT fissuring</td>
<td>35h</td>
<td>93</td>
<td>646</td>
<td>6</td>
<td>341</td>
<td>4*</td>
<td>Flanges WM&amp;HAZ</td>
<td>Eight separate points 35a through 35h. Valero Energy Corporation, private communication to API Subcommittee</td>
<td>After 4 years of service, weld and HAZs of A106 pipe showed cracks.</td>
<td>Points 35a and 35h. These 2 points on the plot represent the range of 8 different failures. After 4.5 to 8 years, 7 different non-PWHT’d carbon steel flanges cracked in the HAZs on the flange side of a flange-to-pipe welds in gasoline hydrotreating service. One cracked on the pipe side of the pipe-to-flange weld. Operating at 645 °F (340 °C) and 57 psia to 94 psia (0.39 MPa to 0.65 MPa) hydrogen partial pressure.</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Non PWHT fissuring</td>
<td>34</td>
<td>120</td>
<td>585</td>
<td>8</td>
<td>307</td>
<td>30</td>
<td>Reactor vessel and piping</td>
<td>J. McLaughlin, J. Krynicki, and T. Bruno, “Cracking of non-PWHT’d Carbon Steel Operating at Conditions”</td>
<td>-</td>
<td>After 30+ years, non-PWHT’d carbon steel reactor, vessels, and associated piping in light distillate hydrotreating service cracked from HTHA. Operating at roughly 580 °F and at 125 psia</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>Non PWHT fissuring</td>
<td>39</td>
<td>136</td>
<td>538</td>
<td>9</td>
<td>281</td>
<td>10</td>
<td>Exchanger shell</td>
<td>Marathon Petroleum Co., private communication to API Subcommittee, 2014.</td>
<td>Hydrotreating service cracked from HTHA. Operating at roughly 580 °F and at 125 psia.</td>
<td>After 10 years, inspection found cracks in non-PWHT’d carbon steel exchanger shell in light hydrotreater service. Operating at roughly 540 °F and at 130 psia.</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>Non PWHT fissuring</td>
<td>40</td>
<td>193</td>
<td>493</td>
<td>13</td>
<td>256</td>
<td>33</td>
<td>Exchanger shell</td>
<td>Marathon Petroleum Co., private communication to API Subcommittee, 2014.</td>
<td>-</td>
<td>After 30+ years, inspection found cracks in non-PWHT’d carbon steel exchanger shell in light hydrotreater service. Operating at roughly 490 °F and at 195 psia.</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>Non PWHT fissuring</td>
<td>37</td>
<td>280</td>
<td>600</td>
<td>19</td>
<td>316</td>
<td>14</td>
<td>Flange HAZ</td>
<td>Phillips 66 Company, private communication to API Subcommittee on Corrosion, 2012</td>
<td>-</td>
<td>After 14 years, non-PWHT’d SA-105 carbon steel flange cracked in the HAZ on the flange side of a flange to pipe weld. Operating at roughly 600 °F and at 280 psia.</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Non PWHT fissuring</td>
<td>38</td>
<td>675</td>
<td>500</td>
<td>47</td>
<td>260</td>
<td>29</td>
<td>Exchanger shell</td>
<td>Total Refining and Marketing, private communication to API Subcommittee, 2011</td>
<td>-</td>
<td>After 29 years, non-PWHT’d carbon steel exchanger shell in HDS service cracked. Operating at roughly 500 °F and at 670 psia.</td>
<td></td>
</tr>
</tbody>
</table>

*service duration taken from Nugent et al. 2017
Table 4 Compositions of various steels identified in the literature that suffered HTHA.

<table>
<thead>
<tr>
<th>Ref</th>
<th>Steel Type</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>V</th>
<th>Cu</th>
<th>Co</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tesoro</td>
<td>SA516 grade 70</td>
<td>0.26-0.29</td>
<td>0.59-0.65</td>
<td>0.23-0.25</td>
<td>0.019-0.031</td>
<td>0.008-0.01</td>
<td>0.10-0.13</td>
<td>0.02-0.03</td>
<td>0.11-0.12</td>
<td>&lt;0.001</td>
<td>0.13-0.18</td>
<td>0.01</td>
<td>0.005-0.01</td>
</tr>
<tr>
<td>Point 19 Ciuffreda and Rowland, 1957</td>
<td>ASTM 201 grade B</td>
<td>0.23-0.24</td>
<td>0.77-0.78</td>
<td>0.10-0.13</td>
<td>0.031-0.033</td>
<td>0.035-0.037</td>
<td>0.08-0.10</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Inglis and Andrews, 1933</td>
<td>Mild steel</td>
<td>0.12</td>
<td>?</td>
<td>0.01&amp;0.07</td>
<td>?</td>
<td>?</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>
Table 5 Correspondence in the API RP 941 file relating to carbon steel that have not been plotted in Figure 1 of the standard according to the technical report API TR 941 (2008).

<table>
<thead>
<tr>
<th>API TR941 Ref No.</th>
<th>HTHA?</th>
<th>Conditions</th>
<th>Duration</th>
<th>Affected region</th>
<th>API TR 941 comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>psi</td>
<td>°F</td>
<td>Bar  °C</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Y</td>
<td>497</td>
<td>650</td>
<td>34</td>
<td>343</td>
</tr>
<tr>
<td>4</td>
<td>Y</td>
<td>Min 160</td>
<td>882</td>
<td>11</td>
<td>321</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max 190</td>
<td>950</td>
<td>13</td>
<td>510</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max 3600</td>
<td>630</td>
<td>248</td>
<td>332</td>
</tr>
<tr>
<td>11B</td>
<td>Y</td>
<td>Min 3600</td>
<td>610</td>
<td>248</td>
<td>321</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max 3600</td>
<td>630</td>
<td>248</td>
<td>332</td>
</tr>
<tr>
<td>19</td>
<td>Y</td>
<td>Min 1595</td>
<td>392</td>
<td>110</td>
<td>218</td>
</tr>
<tr>
<td>20</td>
<td>N</td>
<td>Min 240</td>
<td>675</td>
<td>17</td>
<td>375</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Max 270</td>
<td>750</td>
<td>19</td>
<td>417</td>
</tr>
</tbody>
</table>
Table 6 Data from the laboratory results of Inglis and Andrews, 1933.

<table>
<thead>
<tr>
<th>HTHA level</th>
<th>Test condition</th>
<th>Test duration</th>
<th>Grain size*</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Min 3674 482 253 250</td>
<td>0.14</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Max 3674 518 253 270</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Severe</td>
<td>Min 3674 482 253 250</td>
<td>0.36</td>
<td>50</td>
<td>Decarburisation and inter-granular fissuring</td>
</tr>
<tr>
<td></td>
<td>Max 3674 518 253 270</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>Min 3674 482 253 250</td>
<td>1</td>
<td>10</td>
<td>Fine grained heat treatment prevented HTHA</td>
</tr>
<tr>
<td></td>
<td>Max 3674 482 253 250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>Min 3674 392 253 200</td>
<td>0.34</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Max 3674 428 253 220</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mild</td>
<td>Min 3674 392 253 200</td>
<td>2</td>
<td>50</td>
<td>Slight decarburisation through entire wall thickness. Dense pearlite lamellar structures less affected. Author highlights this as important in respect to heat treatments e.g. annealing at 600-700 may be deleterious.</td>
</tr>
<tr>
<td></td>
<td>Max 3674 428 253 220</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>Min 3674 302 253 150</td>
<td>0.9</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Max 3674 338 253 170</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V.minor</td>
<td>Min 3674 302 253 150</td>
<td>2</td>
<td>50</td>
<td>V. minor attack, slightly decarburised regions extending from surface.</td>
</tr>
<tr>
<td></td>
<td>Max 3674 338 253 170</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Estimated from image in book using the magnification stated. Potentially quite inaccurate depending on any magnification applied during reproduction.
Data associated with the incubation times shown in Figure 3 of APIRP941: 2016 (recreated in Figure 8).

<table>
<thead>
<tr>
<th>API Ref No.</th>
<th>Conditions</th>
<th>Type</th>
<th>HTHA</th>
<th>Affected Region</th>
<th>API RP Ref</th>
<th>API RP Notes</th>
<th>TWI Notes</th>
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</thead>
<tbody>
<tr>
<td>Fig. 1</td>
<td>Fig.3</td>
<td>psi °F Bar °C Servic e Test years</td>
<td>Y/N</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23F</td>
<td>- A</td>
<td>131 621 9</td>
<td>327 11</td>
<td>Y</td>
<td>Hot bent section</td>
<td>Amoco Oil Company, 1960</td>
<td>After 11 years of service, damage was found in the hot bent section of A106 pipe. Unheated straight sections were not affected</td>
</tr>
<tr>
<td></td>
<td>- A</td>
<td>165 624 11</td>
<td>329 10.8</td>
<td>Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- A</td>
<td>299 600 21</td>
<td>316 3.3</td>
<td>Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- A</td>
<td>302 700 21</td>
<td>371 3.1</td>
<td>Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>- B</td>
<td>332 575 23</td>
<td>302 1</td>
<td>Y</td>
<td>Weld toes</td>
<td>Ciuffreda &amp; Rowland, 1957</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- B</td>
<td>367 583 25</td>
<td>306 1</td>
<td>Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>- C</td>
<td>398 574 27</td>
<td>301 2</td>
<td>Y</td>
<td>Various</td>
<td>Zapfe, 1944</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- D</td>
<td>401 800 28</td>
<td>427</td>
<td>0.034 Y</td>
<td>Parent</td>
<td>Allen et al., 1961</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- D</td>
<td>398 999 27</td>
<td>537</td>
<td>0.034</td>
<td>Parent</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- D</td>
<td>892 1000 62</td>
<td>538</td>
<td>0.001 Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- D</td>
<td>911 800 63</td>
<td>427</td>
<td>0.003 Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- D</td>
<td>1399 700 96</td>
<td>371</td>
<td>0.011 Y</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>- E</td>
<td>451 900 31</td>
<td>482</td>
<td>0.032 Y</td>
<td>Parent</td>
<td>Weiner, 1961</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- E</td>
<td>697 1000 48</td>
<td>538</td>
<td>0.003 Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- E</td>
<td>700 900 48</td>
<td>482</td>
<td>0.007 Y</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>- E</td>
<td>700 808 48</td>
<td>427</td>
<td>0.014 Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- E</td>
<td>951 900 66</td>
<td>482</td>
<td>0.003 Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- E</td>
<td>1393 800 96</td>
<td>427</td>
<td>0.004 Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- F</td>
<td>494 598 34</td>
<td>314</td>
<td>0.06 Y</td>
<td>effluent exchanger tube bundle</td>
<td>Hur et al., 1956</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- G</td>
<td>697 950 48</td>
<td>510</td>
<td>0.01 Y</td>
<td>Parent?</td>
<td>Naumann, 1938</td>
<td></td>
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<tr>
<td></td>
<td>- G</td>
<td>700 853 48</td>
<td>456</td>
<td>&lt;0.01 N</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- G</td>
<td>703 753 48</td>
<td>400</td>
<td>&lt;0.01 N</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- G</td>
<td>1400 750 97</td>
<td>399</td>
<td>0.01 Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- G</td>
<td>4200 577 290</td>
<td>303</td>
<td>&lt;0.01 N</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- G</td>
<td>12500 527 862</td>
<td>275</td>
<td>0.63 Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16C</td>
<td>- J</td>
<td>356 591 25</td>
<td>311 2</td>
<td>Y</td>
<td>Various</td>
<td>Evans, 1948</td>
<td>In a series of 29 steel samples, 12 were damaged, while 17 were not</td>
</tr>
<tr>
<td></td>
<td>- J</td>
<td>370 600 26</td>
<td>316 1.9</td>
<td>Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- K</td>
<td>208 700 14</td>
<td>371 8500</td>
<td>Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20A</td>
<td>- L</td>
<td>205 749 14</td>
<td>398 &lt;0.66 2</td>
<td>Y</td>
<td>Parent?</td>
<td>API Refinery Corrosion Committee Survey, 1957</td>
<td>A section made of A106 pipe was found to be damaged to 27% of its thickness after 5745 hours. Other pieces of pipe in the same line were unaffected.</td>
</tr>
<tr>
<td></td>
<td>- M</td>
<td>7000 660 483</td>
<td>349 0.03</td>
<td>N</td>
<td>Class, 1960</td>
<td></td>
<td>In German. No obvious carbon steel values presented.</td>
</tr>
</tbody>
</table>

References work by Newitt and Inglis and Andrews, where temperatures as low as 200°C and 150°C respectively were identified to result in HTHA. Small scale bend specimens (1/16” thick). Investigating effects of steel cleanliness, cold work and influence of pressure and temperature.

Exact incubation times were calculated as the point at which reduction of area of miniature specimens (0.09”/2.3mm) degrade. Claims that surface preparation and thickness will not affect incubation time, as hydrogen ingress is not the rate-controlling step. 800-1100°F at 700psi and 450-950psi at 900°F. No data point for 1400psi was identified in the paper.

The paper refers to a service period of ‘several hundred hours’ The best indication of time is the 6 months mentioned in Fig. 5 of the paper. Nowhere is a service duration of 500 hours mentioned.

Cannnot obtain exact paper. Paper of same year and author in Stahl und Eisen does appear to have some data points that match up, but some that do not. Details of experiment are not understood without translation.

The notes are not translated.
### Table 8 Stages of attack as proposed by Vitovec 1964.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Description</th>
<th>Mechanism</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Build-up of pressure in Sub-microscopic voids (incubation period)</td>
<td>Size of cavities controlled by surface tension</td>
<td>Reversible; rate of expansion or shrinking determined by rate of pressure increase or decrease; rate controlled by surface reactions; no influence on mechanical properties</td>
</tr>
<tr>
<td>2</td>
<td>Growth of cavities</td>
<td>Rate controlled by vacancy diffusion</td>
<td>Reversible; rate of shrinking slower than in stage 1; transition from stage 1 to stage 2 and growth rate influenced by applied stress; influenced by small alloy additions</td>
</tr>
<tr>
<td>3</td>
<td>Growth of cavities</td>
<td>Rate controlled by dislocation creep mechanisms, expansion of cavities to large fissures</td>
<td>Rate is sensitive to stability of carbides, creep strength, and applied stress</td>
</tr>
<tr>
<td>4</td>
<td>Decreasing growth rate of fissures</td>
<td>Rate controlled by diffusion of carbon and the microstructure of the material</td>
<td>Exhaustion of carbon</td>
</tr>
<tr>
<td>5</td>
<td>Partial shrinking of voids</td>
<td>Shrinking of smaller voids by a vacancy diffusion mechanism</td>
<td>Fissures become connected and permit escape of methane; material becomes completely decarburized</td>
</tr>
</tbody>
</table>

### Table 9 Stages of attack as described by Vitovec, 1984 and API941, 2016 for comparison.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Description</th>
<th>Vitovec, 1984</th>
<th>API RP 941, 2016</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methane pressure builds up at sub-microscopic voids along interface boundaries which act as high energy hydrogen traps; methane is balanced by surface tension so growth is slow; reversible with external hydrogen pressure; little effect on mechanical properties</td>
<td>Incubation period during which the microscopic damage cannot be detected with advanced NDE techniques and the mechanical properties are not affected</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>When the cavities reach a critical size they grow rapidly by diffusion processes</td>
<td>Damage is detectable optically (&lt;1000X), possibly detectable by advanced NDE techniques, and mechanical properties are partially deteriorated</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>At a certain size dislocation creep mechanisms become operative and expansion occurs at increasing rates</td>
<td>Rapid mechanical property deterioration associated with rapid fissure growth</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Eventually interconnection of cavities and venting of methane may take place</td>
<td>The final stage where carbon in solid solution is reduced to compromise material mechanical properties to a level where cracking can occur</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1 Process diagram of NHU heat exchangers, showing the flow of tube side feed (blue) and shell side heating fluid from the reactor effluent. The failed Exchanger E is highlighted. CSB, 2014.
Figure 2 Damages identified through NDE and metallurgical sectioning of Exchangers B and E. CSB, 2014.
Figure 3 Reported tube and outlet conditions examined in the CSB report. Note that the pressure ranges were not available for the 3 instances 2008-2009 and so the pressure range for the incident was used in all instances.

Figure 4 Results of CSB modelling exercise, showing the estimated operating envelopes for welds CS4 and CS2, representing the hottest and coldest regions where HTHA was identified. The Nelson curve for welds without PWHT in the 2016 edition of API RP 941 is shown, as well as the limit proposed by the CSB. Reproduced courtesy of the American Petroleum Institute.
Figure 5 Carbon steel Nelson curves in different editions of API RP 941:2016. Reproduced courtesy of the American Petroleum Institute.
Figure 6 Nelson curves from 2016 edition with data points. API RP 941:2016. Reproduced courtesy of the American Petroleum Institute.
Figure 7 Histograms showing the distribution of durations associated with the carbon steel data in Figure 1 of API RP 941:2016. Note, only some data points have durations readily available.

a) Non-welded or welded with PWHT;

b) All carbon steel data (including ‘non-PWHT’ data) with duration data.
Figure 8 Incubation curve according to API RP 941: 2016. Reproduced courtesy of the American Petroleum Institute
Figure 9 Histogram showing the distribution of durations associated with the carbon steel data in Figure 3 of API RP 941:2016 (incubation times).
Figure 10 Results of parametric models produced by various authors overlaid on the incubation curves from API RP 941:2016. Reproduced courtesy of the American Petroleum Institute
Figure 11 Schematic showing the change in measurable attributes during the different stages of attack of a thin specimen exposed to a high temperature hydrogen environment from all sides.

Figure 12 Schematic showing the variation in through wall properties of a vessel subject to HTHA from one side.
Maintaining the integrity of process plant susceptible to high temperature hydrogen attack. Part 2: factors affecting carbon steels

Carbon steel process plant that operates with hydrogen at elevated pressure and temperature can be weakened by a phenomenon known as high temperature hydrogen attack (HTHA). Hydrogen diffuses through the steel and reacts with carbon to form methane which builds up and degrades the steel’s mechanical properties. If this phenomenon is taking place and continues undetected, it can potentially lead to failure of the process plant and a major accident. A fatal fire and explosion at the Tesoro Refinery in the USA in 2010 was caused by rupture of a hydrocarbon containing heat exchanger which had been weakened by HTHA.

HSE commissioned research to give a better understanding of maintaining the integrity of process plant operating in high temperature hydrogen service susceptible to HTHA. The research is described in two reports which should be read together. Part 1, RR1113, gives an analysis of the performance limitations of ultrasonic non-destructive testing techniques when searching for the presence of HTHA, and emerging technologies that may offer improved detection. Part 2, RR1114, discusses factors affecting HTHA for carbon steels including: the safe operating pressure and temperature envelope for plant (‘Nelson Curves’); steel type, welds, stress and other material factors; and equipment operating history.

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