HTHA: RISK AND RESPONSE

Justin Dansbury, Becht, examines methods for identifying high temperature hydrogen attack (HTHA) threats and explores practical risk management via damage progression models.

High temperature hydrogen attack (HTHA) remains a significant damage mechanism affecting hydrogen-containing process equipment operating at elevated temperature and pressure. While the refining industry has historically received the greatest attention regarding HTHA risks, ammonia and syngas facilities face similar threats due to equipment exposure to hydrogen-rich process environments. Equipment designed or installed prior to the publication of the 8th Edition of API RP 941, Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants, may now operate outside the accepted safe operating envelopes.

Table 1. **Summary of input data and assumptions**

Equipment	Methanator	High temperature shift converter
Material	SA-204 Gr. B (CS-0.5 Mo)	SA-204 Gr. B (CS-0.5 Mo)
PWHT	Yes (1150°F 1 hr)	Yes (1100°F 1 hr 50 mins)
Commissioning date	November 1982	November 1982
Current operating hour	361 560 hrs	361 560 hrs
Effective temperature (2003 - 2024)	319.4°C	417.9°C
Effective pH_2 absolute (2003 - 2024)	1.348 MPa	0.831 MPa

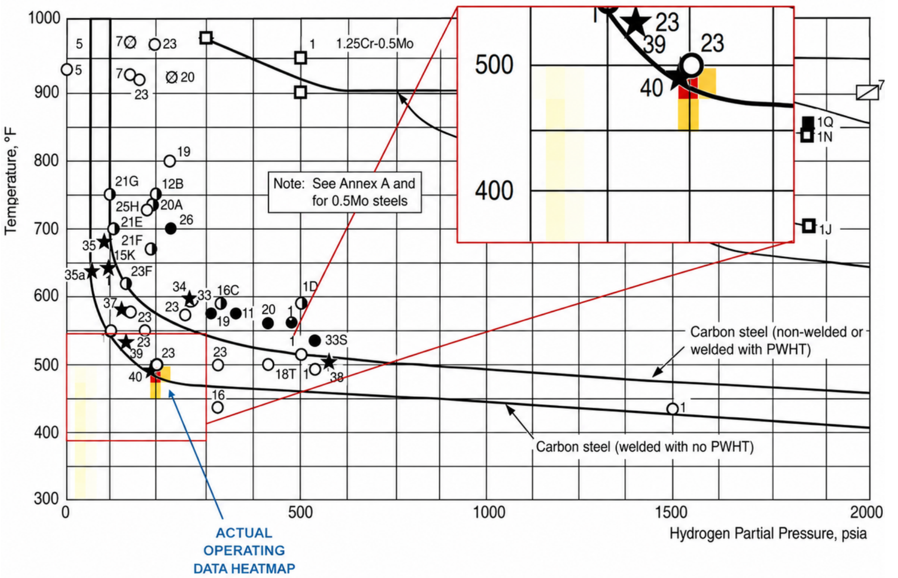

Figure 1. Overlay of actual operating conditions over Figure 1 from API RP 941 8th Edition.

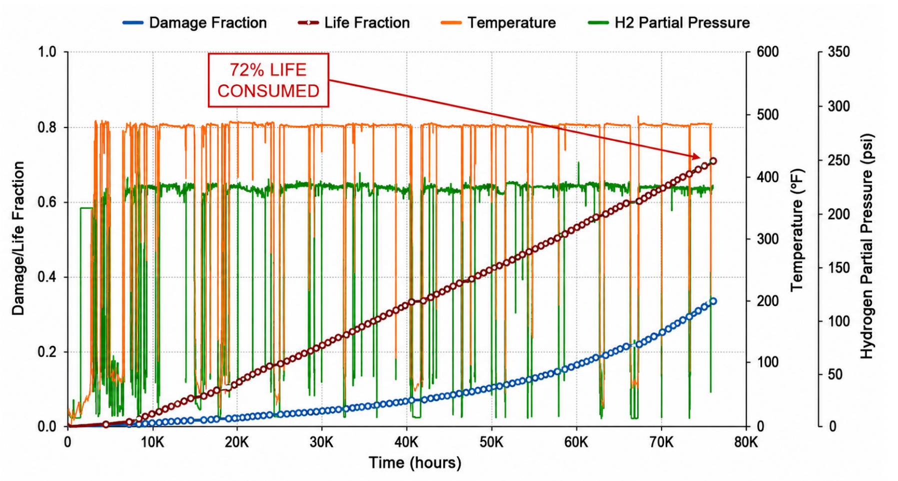

Figure 2. Damage/life fraction calculation calculated with actual operating conditions since commissioning.

This article shares methods for identifying HTHA threats and explores practical risk management via damage progression models. Case studies will be presented using Becht's own HTHA software as a tool in risk management for the following equipment: ammonia converter, methanator, high temperature shift convertor, and various piping circuits in an ammonia plant. This software may also be used to assess cold-wall equipment previously exposed to elevated temperatures because of refractory degradation: steam methane reformer (SMR) outlet headers, transfer lines, waste heat boilers, process gas boilers, and secondary reformers.

Background

HTHA is a complex damage mechanism that has challenged engineers trying to anticipate the degree of damage or service life. HTHA can be thought of as hydrogen-promoted creep damage at temperatures below the typical creep regime. Atomic hydrogen present in the process environment enters the surface of the equipment, diffuses into the subsurface, then combines with carbon present in carbides in the steel to form methane, creating very small bubbles. As pressure builds, the bubbles combine to form fissures, which combine to form cracks.

Evolution of API RP 941 and industry implications

The traditional method by which industry has managed HTHA has been to use experience-based curves (API RP 941 Nelson curves) drawn below the lowest reported case of HTHA attack. These curves have been used in design for material selection and evaluation of existing equipment. The Nelson curves show a temperature/partial pressure hydrogen relationship for each material.

The Nelson curves published within API RP 941 have evolved over time as experience, failures, and laboratory data have become available. The 8th Edition introduced important changes, including reduced operating limits for several commonly used materials.

Note that in the upcoming 9th Edition of API RP 941 time-based curves will be included, introducing lower design limits.

In approximately 25 years, the most significant impacts have been with non-PWHTed carbon steel and C-0.5 Mo steels, including removal of the C-0.5 Mo line in the 4th Edition (1990) and introduction of a lower carbon steel curve for non-post-weld heat-treated (non-PWHT) welds in the 8th Edition (2016).

Table 2. **HTHA life assessment for methanator**

Parameters	Life assessment (minimum material properties)
Carbon activity	0.75
Damage fraction	0.66
Becht model current life fraction	0.84
Total equipment life (25% Wall ID/end of life)	424 200 hrs (48 years)
Calculated remaining life (25% Wall ID/end of life)	62 600 hrs (7.1 years)

Table 3. **HTHA life assessment for high temperature shift converter**

Parameters	Life assessment (minimum material properties)
Carbon activity	0.75
Damage fraction	1.0
Becht model current life fraction	1.0
Total equipment life (25% Wall ID/end of life)	72 700 hrs (8 years)
Calculated remaining life (25% Wall ID/end of life)	0 hrs

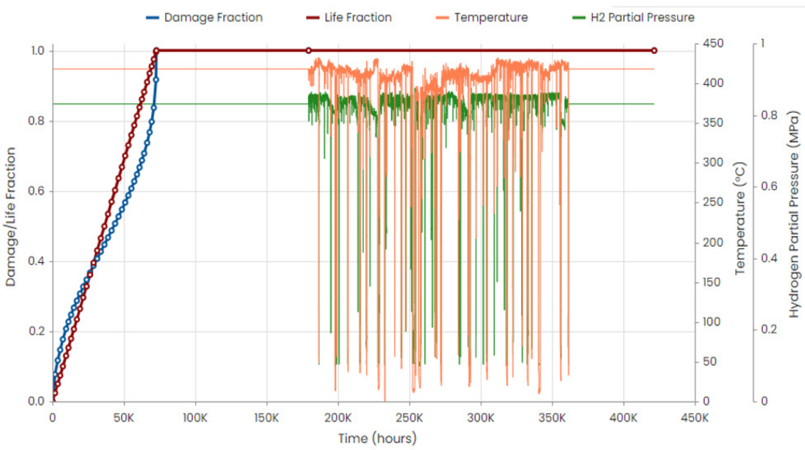

Figure 3. Methanator HTHA daily damage calculator, calculated with minimum material properties (ac = 0.75).

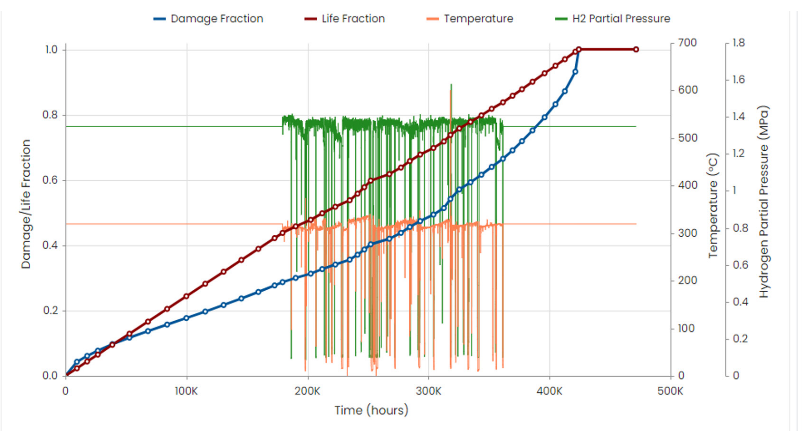

Figure 4. High Shift Converter, calculated with minimum material properties (ac = 0.75).

Retroactive reassessment as a best practice

Retroactive reassessment involves evaluating existing equipment using current API RP 941 design criteria. The objective is not to determine whether equipment lies above or below a Nelson curve, but to establish an understanding of overall risk.

An example framework for HTHA screening may be:

- Trending actual temperature and hydrogen partial pressures (see notes).
- Gather material of construction and PWHT status.
- Compare each equipment operating conditions to the applicable curve depending on metallurgy and PWHT status.
- Screening interpretation:
  - Equipment operating 50°F below applicable Nelson curve or within 50 psia pH_2: no further action.
  - Equipment operating within 50°F or above the applicable Nelson curve: further assessment needed.

Damage progression modelling and risk management

One of the most valuable advancements in HTHA management is the use of damage progression modelling. Rather than treating HTHA susceptibility as a pass/fail condition, modern approaches evaluate the likelihood and potential progression of damage over time.

Damage progression models incorporate variables such as operating temperature, hydrogen partial pressure, time in service, material composition (carbon activity), PWHT condition, process excursions, and inspection findings.

Becht's proprietary HTHA software has been used to support such evaluations by integrating operating data, material information, and damage susceptibility models into a practical engineering framework.

This approach is based on work developed by Gerrit Buchheim, an expert in HTHA, and an analytical model developed by Dave Dewees.[1] The model considers damage accumulation within the material and represents this by a damage fraction. Three parameters are calculated using Becht's HTHA model: life fraction, total equipment life, and remaining equipment life. The life fraction is based on the ratio of operating hours at a given condition to calculated life at that condition.

The time to reach a life fraction of 1.0 near the inner diameter (ID) indicates potential to find macro HTHA damage near the ID. HTHA damage reduces through the wall due to the reduction in effective hydrogen partial pressure. Therefore, equipment may still have significant remaining life beyond the initiation of macro HTHA damage near the ID.

Extensive through wall damage (25% through wall position) is equated to failure in Becht's model and could impact the mechanical integrity of the shell. A life fraction of > 1 at the 25% through wall position (from ID) would indicate the potential for macro HTHA damage in the subsurface material, which has the potential to compromise integrity.

The total calculated equipment life is also provided with a starting point of 0 damage from equipment commissioning. Remaining life is calculated

Table 4. Summary of input data and assumptions

Material			PWHT	Commission date	
SA 302 Grade B; with known Mo/C > 2.5			Yes	1989	
Time period	Temperature basis	Adjusted/operating temperature	H_2 partial pressure (H_2PP) basis	Adjusted/operating H2PP	Notes
Process adjustment (1989 - 2010)	Adjustment applied to historical conditions	+15°C	Adjustment applied to historical conditions	+0.15 MPa	Applied to pre-2010 operating data
1989 - 1998	Base temperature = 255°C	270°C (255°C + 15°C)	Base H_2PP = 10.34 MPa	10.49 MPa (10.34 + 0.15 MPa)	Assumed adjusted operating conditions
1998 - 2010	2010 reference period average = 227°C, SD = 10°C → 237°C + 15°C	252°C	Base H_2PP = 10.34 MPa	10.49 MPa (10.34 + 0.15 MPa)	Assumed adjusted operating conditions
2010 - present	Average = 227°C, SD = 10°C	237°C	Average H_2PP = 9.7 MPa, SD = 1.11 MPa	10.8 MPa	Total operating pressure = 11 MPa; daily and hourly conditions used for calculations
Excursion conditions	Metal temperature during excursions	288°C	Excursion H_2PP	5.2 MPa	Total excursion duration over 10 years = 152 hrs

using the operating conditions as future operating conditions starting from the reported life fraction.

Case study applications in ammonia plants

The following case studies highlight how equipment designed using legacy editions of API RP 941 were screened and risk-assessed with Becht's HTHA software platform.

Case study one: shift converter piping

An ammonia plant was commissioned in 2016; however, the materials selection design basis used the 7th Edition of API RP 941 (published in 2008). Retroactive assessment identified several non-PWHT carbon steel piping circuits which operated at or above the 'carbon steel (welded with no PWHT)' curve (Figure 1).

The operating conditions were then modelled in Becht's HTHA software to identify the likelihood of significant crack-like flaws (i.e., the existence of a 25% deep crack). A carbon activity (Ac) of 1 was used along with considerations for non-PWHT condition. Carbon steel and C-0.5 Mo steel has a wide range of materials performance depending on chemistry, heat treatment, etc. The activity of methane formation (stability of carbides) for HTHA typically ranges from 0.4 - 0.75 for C-0.5 Mo and an Ac = 1 for carbon steel.

The model predicted that approximately 72% of life was consumed and that there was a significant likelihood of flaws after an additional ~20 000 hrs of service. See Figure 2 for model results.

In this particular case study, the client decided to replace the subject piping during a planned outage before the subject piping reached 100% life consumed. No additional inspection was performed.

Case study two

An ammonia plant was commissioned in 1982 with a methanator and high temperature shift converter fabricated with C-0.5 Mo – well before the removal of the C-0.5 Mo curves in the 4th Edition of API RP 941. Retroactive assessment identified that both vessels had operated above the PWHT CS curve.

Methanator

The results of Becht HTHA model with minimum materials properties of CS-0.5 Mo are provided in Figure 3 and summarised in Table 2.

High temperature shift converter

The results of the HTHA Damage Calculator with minimum material properties of CS-0.5 Mo are provided in Figure 4 and summarised in Table 3.

The Methanator and High Shift Converter were determined to be at risk of HTHA damage. The remaining life using minimum material properties was 62 600 hrs (7.1 years). The remaining life of High Shift Converter using minimum material properties was 0 hrs (0 years). Further calibration of the model and longer life can potentially be achieved by taking into consideration carbon activity via actual Mo/C ratios and inspections recognised by API RP 941 (e.g., TFM).

Case study three: ammonia converter

An ammonia plant was commissioned in 1989 with an ammonia converter fabricated with C-0.5 Mo – a year before the removal of the C-0.5 Mo curves in the 4th Edition of API RP 941. From 1989 - 1998 the vessel previously operated at a higher temperature.

Electronic temperature monitoring began in 2010 and from 1998 - 2010 presumably operated at similar conditions to present. A process adjustment is added to account for data uncertainty. These adjustment and assumptions are shown in Table 4.

The subject ammonia converter operated ~287 000 hrs since commissioning in 1989. The life fraction at the ID surface based on the current operating conditions and a carbon activity of 0.5 was calculated to be 0.262 (Figure 5). The ammonia converter was modelled with a favourable carbon activity of 0.5 based on a Mo:C ratio of > 2.5.

The time to reach a life fraction of 1.0 near the ID indicates the potential to find macro HTHA damage near the ID at the current operating conditions is greater than 500 000 hrs.

An analysis was performed with a carbon activity of 0.6, which would indicate a significant increase in material susceptibility to HTHA. Based on these results the life fraction was calculated to be 0.889 (Figure 6) and the time to reach a life fraction of 1.0 near the ID, indicating the potential to find macro HTHA damage near the ID at the current operating conditions is 108 829 hrs.

Sensitivity analysis was also performed around excursion times with a metal temperature of 550°F (288°C), H_2pp= ~750 psia (5.2 MPa) and a duration of excursions over 10 years equal to 600 hrs. This increased the life fraction by less than 5%.

The likelihood based on these conditions is 'very low.' Based on results of the sensitivity analyses and results of the last inspection for HTHA, an inspection was recommended at a shutdown prior to reaching an additional 12 years from the assessment date.

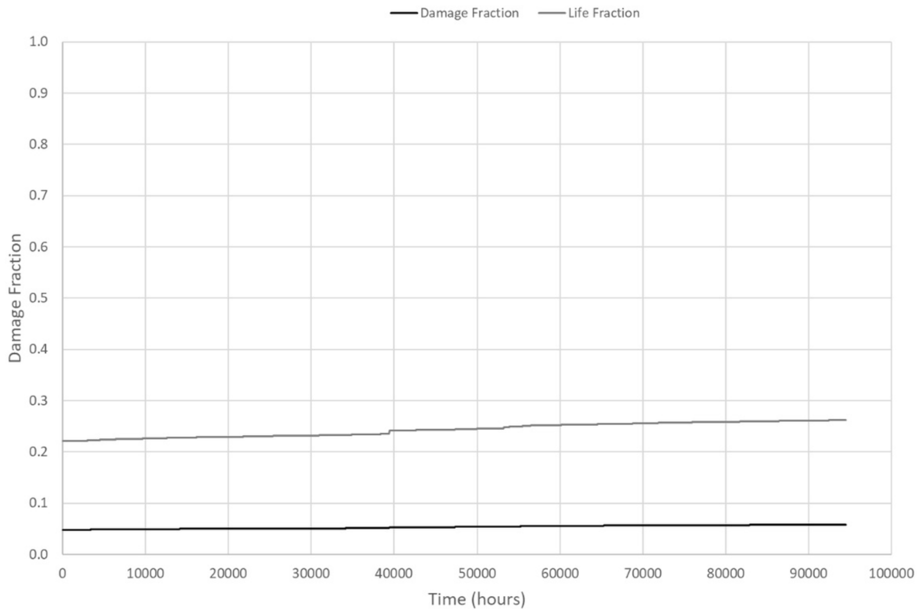

Figure 5. Life fraction with time starting from 9/11/2010 to present at the 0% through wall position with carbon activity of 0.5.

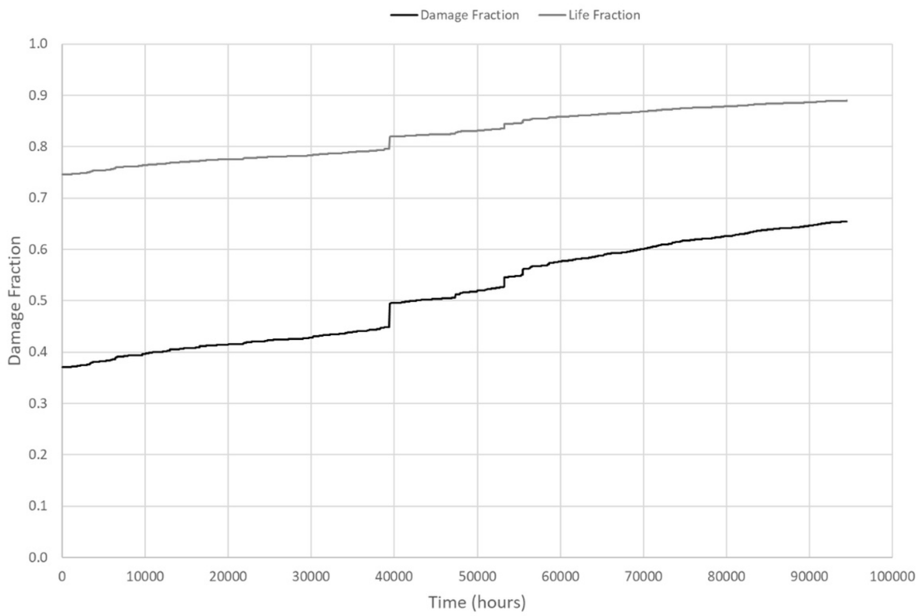

Figure 6. Life fraction with time starting from 9/11/2010 to present at the 0% through wall position with carbon activity of 0.6.

In addition, a recommendation was given to mitigate accelerated damage from excursions: a standard Integrity Operating Window (IOW) at 570°F (300°C).

Conclusions

Equipment operating in hydrogen service should be reassessed against the latest API RP 941 edition, particularly as future revisions are expected to introduce more conservative time-based curves. If equipment exceeds current screening limits, risk should be managed through damage modelling, implementation of integrity operating windows (IOWs) with operator alarms, and risk assessment using operating data, model results, and industry experience. These assessments support decisions ranging from continued operation and future turnaround inspection, to immediate shutdown and replacement. WF

Notes

1) Caution must be applied to heat exchanger stacks where a temperature indicator might not represent worst-case conditions.
2) Calculating H_2 partial pressure in multiphase flow is challenging and should be performed using methodologies provided in API RP 941.
3) Consider all conditions: bypass, shutdown, start-up, end-of-run, etc.

Reference

1. DEWEES, D. "Breakthroughs in Predictive HTHA Life Assessment: Time Dependent Nelson Curves and Inspection Planning Enhancements", *Inspectioneering Journal*, (January/February 2022).