Michael W. Hester, Cherokee Nitrogen, a subsidiary of LSB Industries, Inc., USA, and Daniel J. Benac, Baker Engineering and Risk Consultants, Inc., USA, present an example of HTHA, including an HTHA failure in an ammonia plant, and provide mitigation actions to be taken to reduce the risk of future HTHA failures in other equipment and piping.

REDUCING THE RISK OF HTHA FAILURES

Ammonia plant equipment operates at elevated temperatures and is exposed to environments such as hydrogen that can potentially result in life-limiting conditions. Some of the elevated temperature failure mechanisms common to ammonia plant equipment are: high temperature hydrogen attack (HTHA), metal dusting, nitriding, oxidation, stress relaxation cracking, overheating, and creep.[1] HTHA is one potential life-limiting mechanism that can cause ammonia plant equipment and piping to have a sudden and catastrophic failure. This article presents a classic example of HTHA, including an HTHA failure in an ammonia plant and, most importantly, the mitigation actions taken that reduced the risk of future HTHA failures in other equipment and piping.

Plant case history

In the subject plant, process technology upgrades were commissioned in 2007 that revamped the ammonia converter and synthesis loop for improved plant safety, reliability, and efficiency benefits. Based on the engineering design specifications for the converter revamp, typical header operating temperatures and pressures were revised accordingly, as shown in Table 1.

Approximately 5 years later, during a routine plant start-up on 13 November 2012 at 10 pm, the ammonia converter effluent cooler header piping suddenly ruptured. No fatalities or major injuries occurred, yet the rupture released hydrogen, resulting in a fire and equipment damage that caused plant downtime of approximately 6 months prior to equipment repairs and upgrades for restart. The schematic equipment layout and missing ruptured header are shown in Figure 1 and Figure 2 respectively.

At the time of failure, it was unknown that a section of carbon steel piping was installed in the header of an auxiliary effluent cooler that was added to the primary cooler approximately 40 years prior to the incident (refer to 117-C and 117-CA in Figure 1). As a result, the carbon steel piping was operating above the recommendations for this material as identified in the 8th edition of the API RP 941 curve illustrated in Figure 3.

Based on the 7th edition of the 941 curve for carbon steel, the piping was slightly below the curve prior to the converter revamp. However, after the revamp in 2007 the piping was now operating above the carbon steel curve. As now known from the new 8th edition released in 2016, the previously identified carbon steel curve in the 7th edition reflects the welded condition with post-weld heat treatment (PWHT).[2] As noted in Figure 3, welded carbon steel piping without PWHT would have been operating above the curve before and after revamp of the converter.

The investigation into the effluent cooler header piping rupture determined that the header, shown in Figure 4, had a brittle fracture appearance and failed due to HTHA. Figure 5 shows the microstructure and evidence of HTHA degradation that occurred in the header after 5 years of operation at the revised operating pressures and temperatures.

What is HTHA?

During the development of the ammonia process in the early 1900s, repeated failures of carbon steel pilot plant reactors were observed. Today, it is understood that these failures had the typical features of hydrogen attack.[3] Beginning with research performed in the 1940s, equipment exposed to hydrogen at elevated temperatures had been found to potentially degrade over time.[4] High temperature exposure of carbon and low-alloy steels to high pressure hydrogen leads to a special form of degradation now known as HTHA. This phenomenon is not the same as hydrogen embrittlement, which degrades toughness at low temperatures. HTHA leads to degradation of material properties at elevated operating temperatures.

Like hydrogen embrittlement, HTHA can result in sudden brittle failure, such as what occurred at the plant in 2012. Carbon steel equipment in hydrogen service at pressures greater than 0.8 MPa (100 psig) and temperatures of 230˚C (450˚F) or above are susceptible to HTHA.

Under the influence of certain temperature conditions and hydrogen partial pressure, atomic hydrogen permeates the steel and reduces iron carbide (Fe_3C) in the steel to form methane (CH_4). This process causes decarburisation to occur in the steel. The methane does not diffuse from the metal so its pressure may build and exceed the cohesive strength of the metal, causing fissuring between grains, blisters, and cracks. When fissuring occurs, as shown in Figure 5, the ductility of the metal is significantly and permanently reduced.

The severity of HTHA rises with increasing temperature and hydrogen partial pressure.[5] Some recent HTHA failures were reported to have occurred at welds that were not stress-relieved.[6] API RP 941 curves were modified in 2016 to account for failures in non-post-welded equipment.[2] Figure 3 shows the addition of the carbon steel, non-post-welded curve that was added after this incident had occurred.

Plant incident HTHA analysis and response

After the failure and subsequent root cause identification, a proactive effort was taken to assess the possibility of HTHA

Table 1. Operating conditions before and after revamp

Process parameter	Before revamp	After revamp
Temperature, °F (°C)	450 (232)	490 (254)
Pressure, psig (MPa)	4200 (29.0)	3400 (23.4)
H_2 partial pressure, psig (MPa)	2100 (14.5)	1700 (11.7)

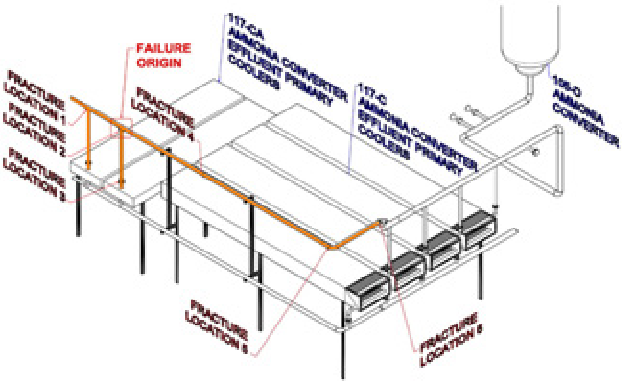

Figure 1. Location of the failure of the fracture in the 6 in. dia. carbon steel header.

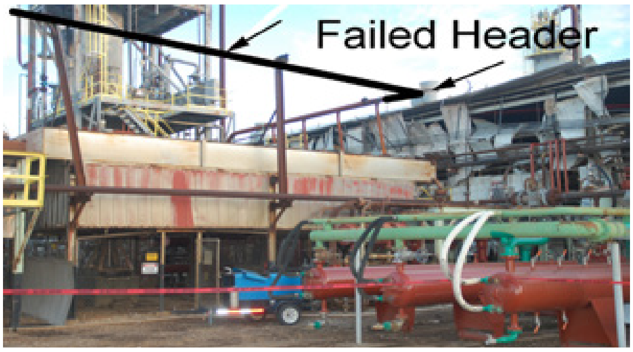

Figure 2. The missing segment of the ruptured 6 in. dia. carbon steel header.

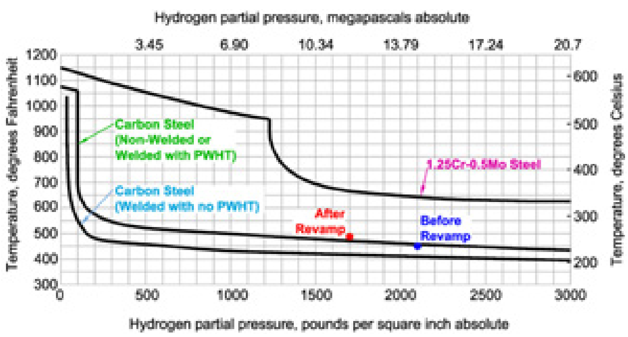

Figure 3. Illustration showing the before and after revamp operating conditions compared to the API RP 941.

degradation in other equipment and to mitigate the potential of future HTHA events. The steps are described as follows:

- HTHA potential: a comprehensive HTHA analysis of equipment operating conditions for temperature, hydrogen partial pressure, materials of construction, and status of heat treatment was conducted. This assessment is essential to understanding potential risk for HTHA failures. The quantitative information for each piece of equipment, piping, or component was then compared to limits on the API RP 941 curves. This comparison determined whether further action – such as additional inspection – was needed.
- Materials of construction confirmation: inspections were performed using positive material identification (PMI) to validate materials of construction for vessels, piping, welds, and ancillary equipment such as valves and fittings. Extensive insulation removal was undertaken to access equipment components to include each shell plate, heads, nozzles, etc.
- HTHA damage assessment and mitigation: based on results from the HTHA analysis and material of construction confirmations, HTHA risk potential was determined by location of equipment on the 941 curves. For example, the delta temperature variance above or below the curve was noted for each piece of equipment's operating parameters. Non-destructive testing (NDT) locations were identified and inspections performed to assess actual potential HTHA damage.
- Material upgrades: based on equipment delta temperature variances above or below the 941 curves as well as results from actual NDT inspections, equipment and piping were upgraded to chrome and moly alloys.

Table 2 identifies typical ammonia plant operating conditions where HTHA could occur given susceptible materials of construction.

Figure 6, Figure 7, and Figure 8 show potential HTHA risk sites for ammonia plant equipment constructed from vintage design specifications utilising carbon steel or other alloys susceptible to HTHA attack.

HTHA prevention – material controls and procedural practices

To prevent elevated-temperature failures, the proper material for the intended operating conditions must be selected and confirmed using PMI. The choice of material is based on the stress, temperature, and environment.

It is also important that the material is not altered, changed, or degraded during operation. An example would be a welding without proper heat treatment. For this reason, quality assurance controls and process monitoring should be in place to reduce the risk of failure.

Atypical operating conditions can also change the local metal wall temperatures. For example, fouling that could occur in a heat exchanger could increase the actual metal wall temperature.

Plant operations should consider the following practices to reduce the risk of HTHA failures:

- Consult with experienced individuals who understand the HTHA phenomenon as well as the API 941 recommended practices.
- Use actual operating temperatures for HTHA susceptibility and validate that the actual operating temperatures and pressures are below the API RP 941 curve by a defined amount.

- Place pressure and temperature indicators at locations that measure the actual operating conditions of equipment that could be susceptible to HTHA.
- Provide definite safe operating limits with necessary process alarms and a response plan for when those limits are exceeded.
- Establish a safety factor approach such as limiting the equipment operating temperature to 50˚F (28˚C) below the API RP 941 curve.
- Perform regular process hazard assessments of operating conditions including changes in pressure, temperatures, or composition of hydrogen.
- Determine whether gradual increases in process production, temperatures, and pressures have occurred, resulting in 'process creep' that may affect materials of construction.
- Evaluate material or operating changes using a management of change (MOC) process with specific considerations for HTHA.
- Evaluate whether temperature excursions have an effect on HTHA susceptibility.

HTHA prevention – inspection practices

Non-destructive examination (NDE) has historically been used to ensure the quality of new fabrication in addition to assessing the integrity of equipment in service. HTHA inspection requires special inspection techniques. Inspection methods used for surface corrosion and wall thinning are not adequate for detecting HTHA since the degradation is a subsurface phenomenon and not readily evident on the surface. The optimum method(s) and frequency(ies) of inspection for HTHA should be determined for specific equipment. Inspection techniques selected should employ methods based on advancing and current technologies that provide enhanced detection capabilities and reliability. They must also be performed by a trained and qualified person in the enhanced detection method.

There have been published recommended inspection techniques for HTHA in the past, yet many owner-users have found notably varying results on the same piece of equipment (raising questions about confidence in the methods to consistently and accurately identify HTHA damage in pressure equipment).[7,8]

Some of the prior and currently used HTHA NDE inspection practices include the following:

- Advanced ultrasonic backscatter techniques (AUBT).
- Phased array ultrasonic testing.
- Time-of-flight diffraction (ToFD).
- High sensitivity wet magnetic particle inspection.
- In situ metallography.

After the incident, comprehensive AUBT and phase array and PMI were performed on equipment and piping.

PMI is a programme that is used to verify that the material in use or intended to be used is the one specified. During fabrication, installation, or maintenance activities, it is possible the wrong materials are substituted. The practice of PMI has identified incorrect materials in hydrogen service. While such mistakes are not a common occurrence, they have resulted in failures often enough to warrant the use of a proactive PMI programme. Do not depend on material certificates alone to validate that the material is correct.

Inspection practices that should be considered, to reduce the risk of HTHA failures and to determine whether HTHA has occurred include:

Figure 4. The brittle fracture of the header due to HTHA.

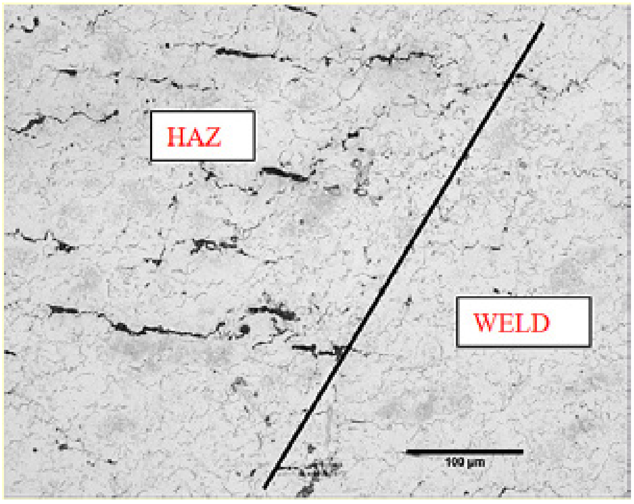

Figure 5. Hydrogen damage observed in the carbon steel line at the heat affected zone (HAZ). Decarburisation and fissuring region caused by hydrogen depleting the iron carbides. (Original magnification: 200x).

Table 2. Typical operating conditions for HTHA

Equipment	Typical temperature, ˚F (˚C)	Typical pressure, psig (MPa)	H_2 partial pressure, psia (MPa)
Ammonia converter outlet	470 – 490 (243 – 254)	3200 – 3400 (22.1 – 23.4)	1600 – 1700 (11.0 – 11.7)
High temperature shift converter	660 – 690 (349 – 365)	215 (1.5)	105 – 110 (0.7 – 0.8)
Methanator outlet	590 (310)	165 (1.1)	11 – 115 (0.1 – 0.8)

- Select inspection methods and establish inspection frequencies that will detect the initial stages of HTHA.
- Ensure written inspection procedures are in place and implemented to provide inspection guidelines and intervals.
- Know the history of the equipment, and if unknown, make sure necessary HTHA inspections are performed.

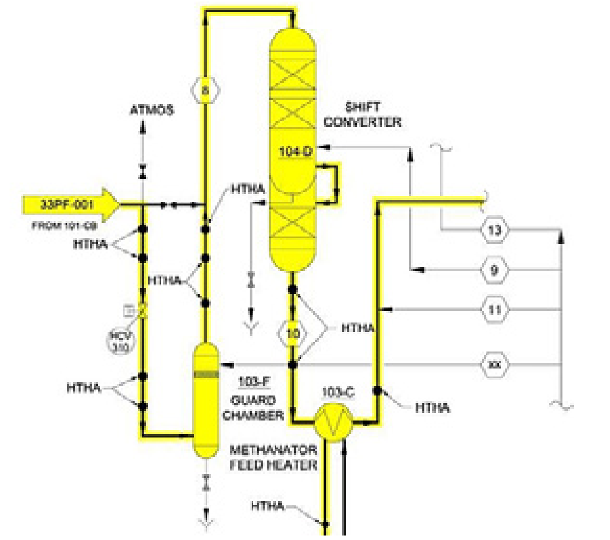

Figure 6. Likely HTHA locations near the high temperature shift converter.

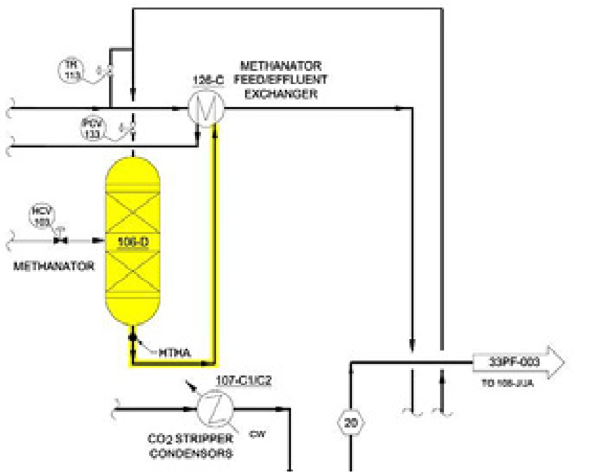

Figure 7. Likely HTHA locations near the methanator.

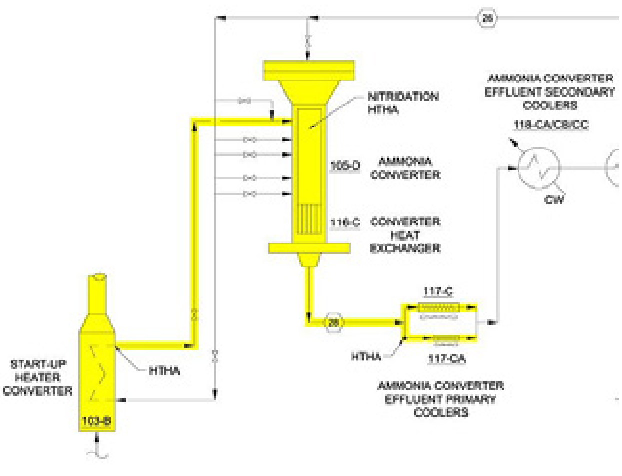

Figure 8. Likely HTHA locations near the ammonia converter.

- Perform base-line retro PMI on all equipment, especially existing equipment that did not have a PMI, constructed of alloy materials, and ensure PMI covers all components as well as welds.
- Perform PMI especially during installation of new equipment, welding of equipment, and during maintenance operations.
- Ensure that proper foundation support for refractory-lined equipment is present to reduce flexure of the refractory.
- Perform regular infrared inspections on refractory-lined equipment, and ensure the operating limit is understood and appropriate actions are taken if the limit is exceeded.
- Document all findings in an inspection programme and follow-up to ensure findings are appropriately acted upon.

Summary

Failure of ammonia plant equipment due to HTHA can occur, especially if an attack happens that is not known of. To reduce the risk of HTHA failures the following should be actively and intentionally pursued:

- Take into account the limitations and possible elevated temperature failure mechanisms when selecting materials of construction.
- Identify whether HTHA is possible and discuss with a knowledgeable resource as part of the MOC process. The MOC process must consider whether process changes will affect the materials and equipment.
- Know and validate the actual operating conditions to determine whether a material is operating in a susceptible range for HTHA, especially if the temperature or pressure increases.
- Select and use the proper and recent HTHA inspection methods using skilled inspectors.
- Employ a proactive inspection programme to ensure the proper material is in place, and whether a material has been altered or degraded.

When proper safety considerations and controls are established, the risk of HTHA failures is greatly reduced for ammonia plants. **WF**

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