Hydrogen Damage Mechanisms Affecting Assets in the Ammonia & Fertilizer Industry[1]

The focus of this paper is to discuss similarities and differences between hydrogen damage mechanisms that can result in equipment failures and costly downtime in ammonia and fertilizer process equipment. The key factors that cause hydrogen embrittlement (HE), hydrogen-induced cracking (HIC), stress-oriented hydrogen-induced cracking (SOHIC), and high temperature hydrogen attack (HTHA) will be discussed with examples of each.

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Ammonia plant equipment operates at elevated temperatures and is exposed to environments such as hydrogen that can potentially result in life-limiting conditions. Ammonia also provides promise as it may provide the source of hydrogen fuel for hydrogen technology. Accommodating increased usage of hydrogen fuel cells using ammonia as the hydrogen source requires increased ammonia production capacity and more global ammonia facilities.[1] Due to increased production and the exposure to hydrogen in process equipment, this increases the potential risk for hydrogen-related damaged to equipment and piping.

Awareness of the hydrogen-related damage mechanisms that can damage equipment is essential in developing the appropriate solution for proper equipment inspection, damage mitigation, and failure prevention. The pertinent damage mechanisms can also provide input for fitness-for-service evaluations as the mechanism and rate of attack needs to be understood to determine the remaining life. For a proper risk-based inspection (RBI) program or during a hazards analysis, the appropriate hydrogen - damaged mechanisms need to be identified so that the probability of failure can be determined in addressing reliability issues.[2]

The following four hydrogen-related damage mechanisms have been observed to affect ammonia equipment, and will be discussed in relation to process variables, process equipment, and materials of construction:

- Hydrogen embrittlement (HE)

[1] 66th Annual Safety in Ammonia Plants & Related Facilities Symposium

- Hydrogen induced cracking (HIC)
- Stress-oriented Hydrogen-induced cracking (SOHIC)
- High temperature hydrogen attack (HTHA)

This paper provides examples and discussion with regard to each type of hydrogen damage mechanism relating to ammonia process parameters, materials of construction and process equipment, and inspection methods and characterization techniques to identify each form of damage. Additionally, useful tips for considering operating envelopes or limits and potential mitigation methods are provided.

Ammonia Equipment Materials of Construction

Most equipment used in the ammonia process production are essentially pressure vessels, piping, and storage tanks whose pressure boundaries are constructed of metallic materials. All materials of construction used in the ammonia industry are susceptible to degradation and various types of damage mechanisms. While it may be possible to select materials of construction that are completely resistant to attack by the process fluids, such an approach can be impractical or cost prohibitive.

Carbon and alloy steels are the most commonly used materials of construction for process equipment in the ammonia industry. These materials offer a suitable combination of strength and ductility and are capable of safely operating in the temperature ranges employed in the ammonia industry. However, carbon and low alloy steels are susceptible to hydrogen damage mechanisms when exposed to a hydrogen environment. Hydrogen may take an atomic (H) or molecular hydrogen (recombined to H_2) form. In either case, only atomic hydrogen (H) diffuses into susceptible alloys such as ferritic steels (C-steel or CrMo alloy steel). The hydrogen molecule (H_2) is too large to diffuse in the steel.

The use of stainless steels in most ammonia plants can reduce susceptibility to hydrogen damage mechanisms. Austenitic stainless steel can also be susceptible if martensite has formed by heavy cold deformation. Titanium sometimes used in equipment has excellent resistance to general corrosion but can form hydrides if in a hydrogen environment.

Comparison of Hydrogen-related Damage Mechanisms for Steel

The hydrogen can be driven into the metal by a corrosion reaction, pressure, partial pressure of hydrogen, temperature, concentration gradient, residual stress, or applied stress in the material. The hydrogen can be in the metal through fabrication, such as in moist welding materials or in a moist welding environment. The microstructure of the material may also influence the location of where the damage may occur. The hardness of a material, weld or heat affected zone is an important factor. There is a hardness limit, often in lower temperature hydrogen damage.

Terminology describing hydrogen-related damage mechanisms can be confusing, inaccurate, or unclear. To identify similarities and help clear up the differences, the four common hydrogen damage mechanisms are described in Table 1. These hydrogen-related damage mechanisms can all occur in Ammonia Process equipment. Table 1 provides an overview and comparison of each type of damage mechanism for steel and alloy steels, including the form the hydrogen takes, description, key parameters, and key mitigation recommendations. This table was compiled for the Ammonia and Fertilizer joint industry program (JIP) by OCI resources collaborating with BakerRisk.[3]

API RP 571 provides general guidance as to the most likely damage mechanisms affecting common alloys used in the refining and petrochemical industry and is intended to

introduce the concepts of service-induced deterioration and failure modes. However, as the API standards tend to focus on refining and hydrocarbon processes, the high pressure and temperature conditions in ammonia and methanol production provides a wealth of experience and knowledge base for hydrogen damage mechanisms. This combined experience provides information that can be utilized by plant inspection personnel to assist in identifying likely causes of damage, to assist with the development of inspection strategies, and to help identify monitoring programs to ensure equipment integrity.

Damage Mechanism	Hydrogen Form	Description	Key Parameters	Mitigation Strategies
Hydrogen Embrittlement (HE)	Atomic	Diffusion of hydrogen atoms into steel, which tend to migrate to voids and dislocations, applying pressure to interior of material, and pinning dislocation motion. Results in brittle behavior. Typically occurs at temperatures below 150°C (302°F), following welding, plating, or submerged cathodic protection; when hydrogen is produced; or during elevated temperature service (>200°C) (392°F) when hydrogen cannot diffuse out of steel and is then cooled (shutdown and subsequent startup).	• Strength and hardness • Residual stress • Material microstructure, e.g., heat affected zone • Atomic H-concentration in the steel after charging hydrogen during elevated temperature service.	• Limit steel hardness to <237 HB/HRC 22 or use lower strength steel • Hydrogen bake-out at 204°C (400°F) following weld processes • Allow outgassing of the steel during shutdown, i.e., lower the cooling rate and be aware of Minimum Pressurization Temperature curves.
Blistering and Hydrogen Induced Cracking (HIC)*	Molecular	Exposure to hydrogen environment or wet H_2S (hydrogen produced during formation of FeS). Hydrogen enters in atomic form, but damage occurs after H-atoms recombine to H_2 molecules inside alloy. Blistering and HIC are strongly affected by the presence of inclusions, laminations (both found in "dirty" steels), and internal discontinuities, all of which provide sites for hydrogen accumulation.	• Hardness and strength • Residual stress • Temperature • Corrosion reaction with formation off atomic Hydrogen (such as H_2S) • Low impurities in the steel composition • Surface scales and inhibitors	• Limit steel hardness to below 237 HB/HRC 22 • Use of protective lining in H_2S environment • Chemistry and manufacturing methods can affect susceptibility and can be modified to produce HIC resistant steel (refer to NACE 8X194).
Stress-Oriented Hydrogen Induced Cracking (SOHIC)*	Molecular	Similar to HIC but cracking occurs in a sufficiently high stress field. Blisters or cracks stacked on top of one another and link up through the cross sectional direction (e.g., stair-step cracks).	• Same as HIC • Stress level applied to alloy	• Same as HIC • Lower stress level, if possible • Post-weld heat treatment
High Temperature Hydrogen Attack (HTHA)	Atomic	Diffusion of hydrogen into steel at elevated temperatures((>200°C) (392°F). Hydrogen reacts with carbides at elevated temperatures to form methane gas. Micro voids, grain boundary voids and micro fissures are generated. Buildup of methane pressure can result in blistering, degradation, and fissures within metal.	• Refer to most recent edition of Nelson curves in API RP 941 • Operating temperature • Partial pressure of hydrogen • Material selection	• Monitor pressure, hydrogen partial pressure, and temperatures • Operate with a safety margin, e.g., 28°C (50°F), below the Nelson Curve • Post-weld heat treatment at sufficiently high temperatures that allow stable carbides to form • Use higher alloyed steels

**Note: HIC and SOHIC are mainly related to feedstocks containing H_2S. They can occur in the gas cleaning section where H_2S is removed (i.e., before the "normal" ammonia plant equipment). After the desulfurization vessels, the amount of H_2S is generally too low to cause HIC or SOHIC.*

Table 1. Comparison of Hydrogen-related Damage Mechanisms for Steel

Hydrogen Embrittlement

Hydrogen embrittlement (HE) is the process by which various metals, most importantly high-strength steel, become brittle and fracture following exposure to hydrogen. Hydrogen embrittlement is often the result of unintentional introduction of hydrogen into susceptible metals during forming or finishing operations such as welding and plating.[4]

The mechanism starts with lone hydrogen atoms diffusing through the metal. At high temperatures, the elevated solubility of hydrogen allows hydrogen to diffuse more easily into the metal (or the hydrogen can diffuse in at a low temperature, assisted by a concentration gradient). The hydrogen atoms pin the dislocations in the steel, especially at the tips of cracks and internal defects. This results in limited moveability of the dislocations and brittle behavior of the steel. High-strength and low-alloy steels and nickel and titanium alloys are most susceptible. Also, CrMo steels that have not been properly post-weld heat treated are susceptible. High hardness zones appear due to the formation of bainite or martensite.

During high temperature service the steel can be charged/loaded with hydrogen. When the process is taken out of service, hydrogen may get trapped inside the crystalline structure of the steel, especially for thick-walled components.

Key Parameters and Factors:

- Hydrogen must be present at a critical concentration within the steel and/or alloy.
- Increased risk where equipment temperatures are high, which can increase the solubility of hydrogen in the material.
- The strength level and microstructure of the steel/alloy must be susceptible to embrittlement. High strength steels above 237 HB/22 HRC are particularly sensitive to HE and can suffer delayed cracking before use due to the presence of hydrogen and residual stresses. Steel and welds with hardness of less than 237 HB/22 HRC is not generally considered susceptible to hydrogen embrittlement.
- A stress above the stress threshold for HE must be present from residual stresses and/or applied stresses.
- HE cracking can initiate sub-surface, but in most cases is surface-breaking.
- HE occurs at locations of high residual or tri-axial stresses (notches, restraint) and where the microstructure is conducive, such as in weld HAZs.
- In higher strength steels, cracking is often intergranular (may be transgranular) and can start subsurface.
- Welding – If wet electrodes or high moisture flux weld electrodes are used, hydrogen can be charged into the steel. Improper PWHT or non-post weld heat treated welds in pipes and vessels are susceptible.
- HE is most pronounced at temperatures between ambient to about 150°C (300°F) because the atomic hydrogen can diffuse at the elevated temperature (i.e., the hydrogen is mobile).

Ammonia Equipment Concerns:

- Syngas coolers
- BFW heaters
- Ammonia Equipment:
- Methanation
- Secondary Reformer and Heat Recovery

Mitigation Options:

- Use low hydrogen dry electrodes during welding and preheating methods.

- Bake electroplated steel components at temperatures of 190 to 220°C (375 to 430°F) within a few hours after the electroplating process.
- Use lower strength steels and reduce residual and applied stresses to avoid fracture due to hydrogen embrittlement.
- Apply proper post-weld heat treatment and reduce the hardness below 225-250 HV
- Allow outgassing of the hydrogen out of the steel by applying a proper (slow) cool-down procedure

Hydrogen Embrittlement Examples

Example 1: Syngas Circulation Boiler

Background: A 13CrMo44 (1Cr-0.5 Mo) Connection pipe between the syngas circulation boiler/economizer and the hot cross exchanger leaked after six years in service. Internal cracking and a leakage in the intrados of the pipe bend was determined on the transition of pipe to weld, as well as cracking in the extrados of the bend on the transition of bend to weld, shown in Figure 1. The Syngas, (H_2, N_2, NH_3) temperature was 320-340ºC (608-644ºF) and the pressure 190-215 bar (2.7-3.1 ksi). The hydrogen partial pressure (pH_2) = 115 bar(a) (1.69 ksi)

Findings: The failure mechanism was hydrogen embrittlement: cracking causing a brittle condition. The steel pipe wall was charged with atomic hydrogen during normal operation at high temperature, and the hydrogen got trapped inside of the metal structure as the pipe wall cooled down during shutdown. This led to loss of ductility and brittle behavior of the pipe material.

The hardness of the weld and the heat affected zone are relatively high (> 225 HV) for a hydrogen loaded pipe, which makes the construction vulnerable to hydrogen embrittlement.

The crack initiated on the inner surface along the weld fusion line and had a transgranular character, propagating towards the outer surface, showing many non-oriented hairline cracks and a staggered propagation. This is typical for hydrogen cracking.

The internal stress due to faulty assembly combined with a relatively high hardness and notch effect of the weld (high-low) under the given shutdown process conditions led to brittle cracking.

Most of the spring supports were out of range, which resulted in improper balance of stress under process conditions. No inspection on pipe supports had been conducted.

It appeared that not all the spring supports had been fixed properly while reconstructing the line, resulting in a fitting piece which had incorrect dimensions. Pipe and elbow were lined up using chain hoists before welding to correct for significant misalignment. This led to high internal stress at the weld position.

Mitigation Options:

The following options were considered:

- Create a maintenance program for spring posts and pipe supports, replacing faulty and/or non-readable devices; and performing regular inspections when the spring pot is within its range.
- Review/extend the applicable Engineering Practice along with training and follow-up with regard to the contributing factors for Hydrogen Embrittlement and what measures should be taken concerning the welding process to reduce the risk of Hydrogen Embrittlement. This should also ensure that a designated engineer becomes owner of the entire modification process, supervising all steps of the change when welding in a hydrogen-loaded system becomes necessary, to ensure compliance with all rules.

- Make sure that the correct pressure and heating/cooling procedures for hydrogen loaded systems are applied in all operating procedures. Applicable SOP's need to have specific maximum allowable depressurization rates related to the remaining equipment temperature for each situation based on the specific applicable damage mechanisms.

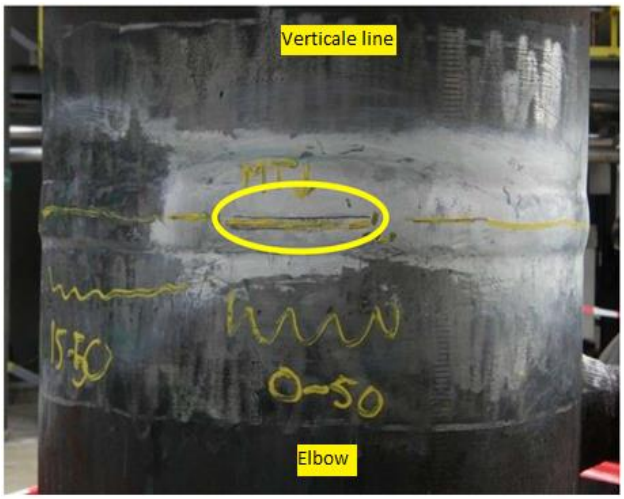


Figure 1. Connection pipe showing the location of cracking at the weld

Example 2: Thermowell Example

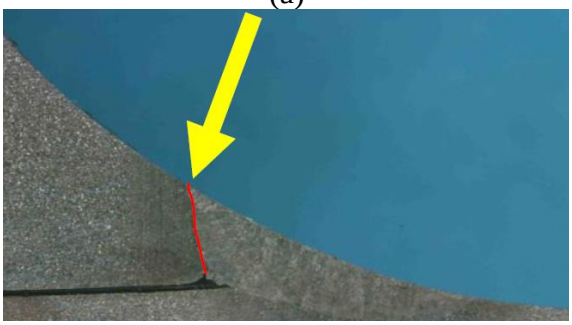
Background: After 48 years of service, a leak was detected in the start-up heater during normal operations because of flames coming out of the line insulation near the thermowell, shown in Figure 2. The Plant was shut down immediately. Syngas leaked through a 30 mm crack in the heat affected zone of the socket weld on the thermowell. The material of the pipe was 10 CrMo 9.10 and the thermowell was 13 CrMo 44. The weld was a mixture of both materials. The normal operating temperature was from 0 to 460ºC (32 to 860°F) and with a pressure of 195 to 215 bar 195-215 bar (2.8-3.1 ksi).

Findings: The crack was of a trans-crystalline character, showing a staggered propagation. The hardness of the material close to the crack was 295 to 380 HV, relatively high but within allowable range. During the 48-year lifetime, Hydrogen-induced cracks formed along the hardest material in the heat affected zone (HAZ) and gradually increased until failure.

Mitigation Options:

- Post-weld heat treatment for welds in hydrogen loaded systems until the hardness is below 320 HV.
- Review of SOP's to control temperature gradients as much as possible.

(a)



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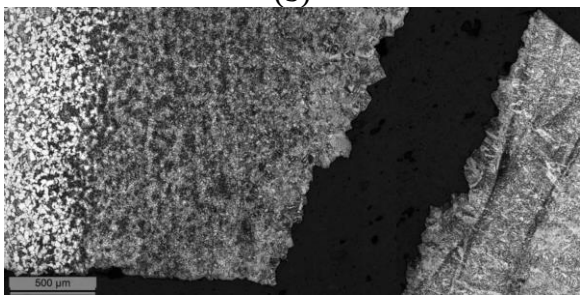

(c)

Figure 2. (a) Socket welded Thermowell; (b) Crack in HAZ; and (c) Transgranular cracking

Example 3: Titanium Hydride

Titanium can be very susceptible to titanium hydride formation. Titanium parts that absorbed hydrogen at elevated temperatures can form hydrides upon cooling. These hydrides lead to a decrease in the strain to failure, loss of strength, and ductility. Hydrogen absorbed when present above specification can result in metal embrittlement, hardening, cracking, and spalling due to the formation of hydrides in the metal.

Background on the Equipment: The titanium 3Al-2.5V float was in the ammonia unit.[5] The titanium float system is a magnetic level indicator that consists of a chamber and a magnet-equipped titanium float that raises and lowers with the fluid level. Operators reported problems with the float and erroneous level readings to site supervision. The titanium float (shown in Figure 3) was removed for investigation and was found cracked, as shown in Figure 4.

Figure 3. The titanium float

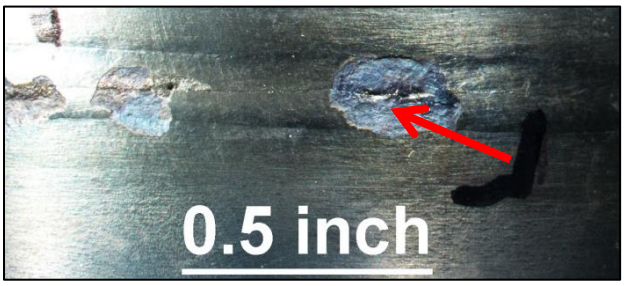

Figure 4. Close-up of the weld showing cracks

The typical operating temperature was 133 °C (271 °F), the typical pressure was 2.8 MPa (400 psig), and the process medium included: Water 10.4%; Hydrogen 54.7%; Nitrogen 18.3%; and CO_2 15.9%.

Findings: Metallurgical analysis determined that the cracking and spalling of the titanium float was due to the excessive pickup of hydrogen, which resulted in the formation of embrittling titanium hydrides.[5] The gas analysis of the weld region showed absorption of excessive amounts of hydrogen at the weld and heat affected zone. The weight percent of hydrogen was as much as 0.479% in the weld compared to 0.015 wt.% in the non-cracked sheet metal.

The most likely source of the hydrogen was from the operation in a hydrogen, steam, and ammonia environment. The areas where the most hydrogen was absorbed were at the weld and weld heat affected zones, likely due to residual stresses. These regions were also harder.

Figure 5 shows the affected weld and HAZ.

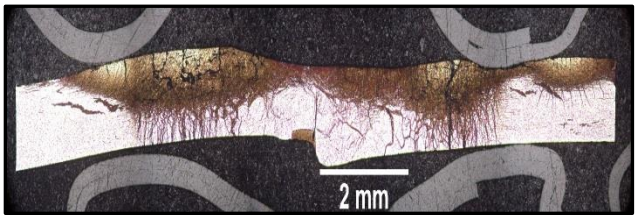

Figure 5. Cross section through the weld and HAZ showing the cracking and hydrides

Mitigation Options:

- Because the titanium absorbed hydrogen, action was taken to include a design change by applying a PTFE (Teflon-like) coating over the titanium float to prevent cracking from occurring. While the manufacturer provided a replacement titanium float with a PTFE coating, this coating may not be protective enough. Other more suitable metals could have been considered for replacement. It is best to keep titanium away from areas with high ammonia concentrations due to titanium's affinity for nitrogen and hydrogen.

HIC and SOHIC

Hydrogen-induced cracking (HIC) and stress-oriented hydrogen induced cracking (SOHIC) are related. Both occur from the presence of hydrogen or from corrosion where hydrogen is liberated and diffuses into the steel, such as with Wet H_2S corrosion. Hydrogen blisters may form as visible surface features or within the material. These blisters may be in arrays. HIC is a potential problem, mostly in low alloy steel weldments, and especially equipment fabricated in the 1960s that has high hardness and/or high levels of impurities and segregations.[6]

SOHIC occurs when these arrays of cracks are stacked on top of one another, usually in the base metal adjacent to the heat affected zone (HAZ).[7] This often occurs at high localized applied or residual stresses.

Key Parameters:

- HIC occurs at locations of high residual or tri-axial stresses (notches, restraint) and where the microstructure is conducive, such as in weld HAZs. Explosion cladding will generate high stresses.
- Hydrogen partial pressure
- Higher hardness alloys or local areas in welds are more susceptible to HIC and SOHIC
- Proper PWHT is required to ensure lower hardness is obtained
- Manual welds made with moisture in the electrodes
- Increasing H_2S potential and temperature increases the available hydrogen. Blistering has been observed between ambient and 150 °C (300 °F).

Ammonia Equipment Concerns:

Some of the equipment below could be susceptible, but the most likely concern for HIC or SOHIC would occur in H2S removal section of the plant.

- Ammonia converter
- Loop waste heat recovery
- Startup Heater Coil
- Shift Converter (moisture in electrodes)
- SynLoop
- Methanation
- High and Low Shift
- Syngas Compression
- Mol Sieves

Mitigation Options:

- Carbon steels should be controlled to keep the weld hardness below 200 HB. Localized areas of hardness above 237 HB can be susceptible.
- Temper or PWHT procedures should be carefully followed and documented. Hardness testing with follow-up PWHT should be performed if hardness levels exceed recommendations.
- Some designers are moving away from Vanadium steels due to difficulty with fabrication.
- Where possible, conduct a furnace stress relief (instead of a local stress relief).
- If necessary, use alloy cladding to protect the steel from the H_2S corrosion.
- Use clean steels, like so-called HIC-resistant steels (NACE 8X194)

High Temperature Hydrogen Attack (HTHA)

High Temperature Hydrogen Attack (HTHA) is a form of degradation caused by hydrogen reacting with carbon to form methane in a high temperature environment.

$$C + 4H \rightarrow CH4$$

When steel is exposed to hydrogen at elevated temperatures, hydrogen will diffuse into the alloy and react with carbon to form cavities/voids filled with methane.[8]

The methane is trapped in these voids and does not diffuse out of the metal. Over time, more and more methane is formed, forming more cavities at the grain boundaries. These cavities coalesce and form micro-cracks at the grain boundaries, which later will grow into macro-cracks. An example of such fractures can be seen in the microstructure of a pipe weld in Figure 6,[9] which shows a decarburization and fissuring region caused by hydrogen depleting the iron carbides. The cracks lower the rupture ductility and fracture toughness, which may result in brittle fracture. The brittle behavior of the material can result in a catastrophic brittle fracture of the asset [10-12] during startup or shutdown excursions.

Susceptible materials include plain carbon steels, C-½Mo Steels, and other low alloy steels and non-post weld heat treated (PWHT) welds. API RP 941 provides guidance to aid in materials selection for fixed equipment operating in environments with hydrogen partial pressures at elevated temperatures and pressures.[13] This guidance can also be useful to materials engineers and process engineers alike, as knowledge of both process conditions and the materials of construction will provide information on an asset's susceptibility to this particular damage mechanism.

The most obvious equipment concerns are any equipment exceeding normal operating temperatures or operating window limits, specifically carbon and low alloy steel vessels and piping operating at temperatures that are above the API 941 RP Nelson curve values. These exceedances may not occur during normal operation, but during startup, shutdown or upset conditions. Catalyst changes, fouling, and flow irregularities may also produce localized areas in exceedance of the recommended limits. Aging plants should be mindful of API RP 941 Nelson Curve operating point changes and should determine whether process changes or HTHA mitigation strategies may be implemented. HTHA is not a concern in solid stainless steel vessels. API RP 941 recommends not to take credit for the presence of a stainless steel cladding or weld overlay when selecting the base metal for a new vessel.

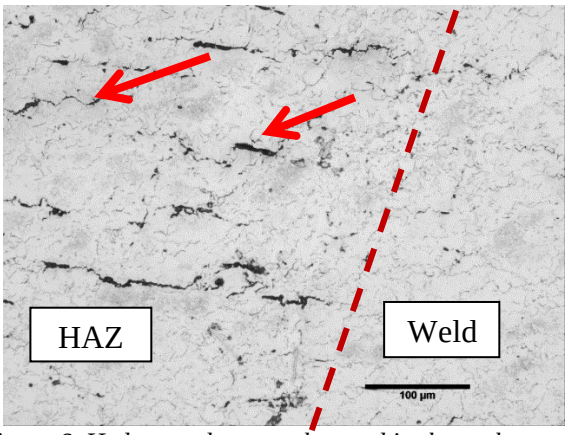

Figure 6. Hydrogen damage observed in the carbon steel line at the heat affected zone (HAZ). Nital etch. (Original magnification: 200x).

Hydrogen content is high in the ammonia process streams, and so it is important to evaluate the potential for HTHA where the temperatures rise above 204°C (400°F) for carbon steel materials. The hydrogen content should be considered on a wet gas basis.

Typical HTHA concerns start with the Shift Unit and equipment through the Ammonia Synloop where temperatures are above 204°C (400°F). However, HTHA may be present in other areas such as secondary reformer pressure shells where refractory failures allow higher shell temperatures. HTHA can also be a concern throughout the ammonia process, including equipment in the following units: Shifts (both high and low shift), Methanation, and SynLoop. SynLoop equipment, particularly converters without furnace stress relief or operating at high temperatures, and startup heater coils are also a

vulnerable point for attack. Additionally, hot spots in secondary reformer and waste heat boilers, Mol Sieves, and pressure envelopes where refractory failures occur are also a concern.

Key Parameters:

- Non-post weld heat treated steels are more susceptible.
- Operating temperatures within, e.g., 28°C (50°F) of the API RP 941 curve values make the material more susceptible due to measurement capability.
- Environmental conditions: Hydrogen partial pressure and operating temperatures as susceptibility to attack increases as H_2 partial pressure increases.
- Materials with an inadequate safety factor using the API RP 941Curve.
- Material substitutions with a wrong material or welding rods and equipment that are not inspected by PMI.
- Material substitution can also happen during maintenance activities when, e.g., bends before and after heat exchangers are accidently mixed up (same dimensions, different steel)
- Exceeding normal operating temperatures or operating window limits.
- Refractory-lined vessels or refractory protected nozzles/pipes where refractory has been compromised (hot spots).
- Aging plants that have inadequate information on API RP 941 Nelson Curve changes, especially for C-½Mo steel and non-PWHT'd carbon steel.
- Stainless Steel-lined vessels with the possibility of hydrogen getting behind the liner.
- Carbon Steels and Low Alloy Steels at operating temperatures that are above the API 941 RP Curve values, including processes that stray outside of the target IOW.

Equipment Concerns:

Aging vessels in particular are subject to HTHA and other hydrogen mechanisms because of their years of service, potential operating excursions, and initial materials selection. The methanator is a high temperature vessel that is subject to temperature excursions and is a candidate for HTHA along with the other methanation unit equipment. There have been reports of progressive degradation when HTHA is found in methanators, with the most notable damage on the bottom of the vessel, which experiences higher temperatures. HTHA damage should be monitored, and a Fitness for Service (FFS) considered to ensure integrity is maintained.

SynLoop:

HTHA is a concern, particularly after a retrofit increases the ammonia conversion, which raises the outlet temperatures of the converter and the downstream equipment. Retrofit heat and material balance predictions may underestimate the temperatures for fresh catalyst, resulting in HTHA conditions for existing materials. Sometimes risk is difficult to identify as temperatures can be unknown due to a lack of instrumentation.[9]

Ammonia Equipment Concerns:

- Hydrogen content is high in the ammonia process streams, and so it is important to evaluate for HTHA potential where the temperatures rise above 204°C (400°F) for carbon steel and low alloy materials.
- The hydrogen content should be considered on a wet gas basis, which may reduce the risk susceptibility for equipment prior to process condensate removal at the CO_2 Purification.

- Typical concerns start with the Shift Unit and equipment through the Ammonia SynLoop where temperatures are above 204°C (400°F).
- However, HTHA may be present in other areas such as secondary unit pressure shells due to refractory failure.

Mitigation Options:

One of the most critical ways to mitigate the potential for HTHA is for plant engineering to review plant processes, the design basis or Form U1 Manufacturer's Report which includes the materials of construction, and operating conditions to identify potential HTHA risks with hydrogen-containing equipment. An important component of this includes conducting an engineering review of pressure, hydrogen partial pressure, and temperatures. Operating with safety margins, e.g., 28 °C (50°F) below the API RP 941 Curve, can also provide additional assurance. Engineering should establish integrity operating limits for all vulnerable equipment. Having an active PMI and retro PMI program is also an essential mitigation component.

If possible or feasible, aging plants should consider replacing equipment with higher alloyed material that are less susceptible to HTHA according to the API RP 941 Curve for desired operating conditions. This review should include determining whether welded equipment or piping was post-weld heat treated, and if not known, assume non-post weld heat treated welds and operate at lower temperature and pressures. One may also consider performing PWHT during the next opportunity. Installing temperature indicators at critical locations, to monitor actual temperatures, and performing regular thermography measurements can help to ensure operating windows and limits are not exceeded or can be addressed.

- Review plant to identify potential HTHA risks with hydrogen-containing equipment.
- Perform regular thermography measurements.
- Have an active PMI and retro PMI program.
- Operate within safety margins, e.g., 28 °C (50°F) below the API RP 941 Curve.
- Review quality of past repairs and ensure PWHT practices did not introduce an HTHA risk.
- Determine whether welded equipment or piping is post-weld heat treated. If not known, then assume non-post weld heat treated and operate at lower temperature and pressures. One may also consider performing PWHT during the next opportunity.
- Replace equipment with higher alloyed material that is less susceptible according to the API RP 941 Curve.
- Install temperature indicators at critical locations to monitor actual temperatures.
- Conduct engineering review of pressure, hydrogen partial pressure, and temperatures.
- Set up integrity operating limits for equipment.
- Recheck IOW's in conjunction with process changes where temperatures are affected, such as SynLoop converter retrofits for higher efficiencies.

HTHA Example:

Background: An investigation conducted into a carbon steel effluent cooler header piping rupture, installed in an ammonia converter and synthesis loop, occurred 5 years after a change in operating conditions.[14] The process temperature was increased from 232 to 254 °C (450 to 490 °F), and the operating pressure was decreased from 29.0 MPa (4200 psig) (0.1 MPa (2100 psig) hydrogen partial pressure) to 23.4 MPa (3400

psig) (0.8 MPa (1700 psig) hydrogen partial pressure).

Findings: This process change placed the carbon steel pipe above the API RP 941 Nelson curve temperature for carbon steel at the corresponding hydrogen partial pressure. The piping rupture was found to have a brittle fracture appearance. Failure analysis revealed that HTHA was the damage mechanism that caused the pipe rupture. This example case demonstrates the vulnerability of this portion of the ammonia process if material limits are exceeded and how process changes can create the potential for eventual failure.[14]

Mitigation options considered:

- Conducted Hydrogen damage review of equipment.
- Replaced piping with higher alloy material.

Inspection Methods

For HE, HIC, and SOHIC, some common inspection methods such as those listed below can be used:

- Penetrant testing (PT)
- Magnetic particle testing (MT)
- Wet fluorescent magnetic particle testing (WFMT)
- Ultrasonic testing (UT)
- Radiographic testing (RT)

For volumetric (through wall thickness) HTHA inspections, the previous suggestions found in API RP 941 Annex E will be discontinued and replaced with API RP 586 (in balloting process at this time). It has been demonstrated that the historical methods have been supplanted by more advanced modalities of the Ultrasonic Testing methods found in API 586. These include Advanced Phase Array (using 64 Element Arrays), Total Focusing Method (TFM) or Full Matrix Capture (FMC), Time of Flight Diffraction or a combination of these methods. As always, these methods are strictly dependent on the technique and skill level of the inspector. There is a recognized training and certification program for these methods to qualify and maintain personnel competency.

Inspection methods that can identify potential regions of HTHA are:

- High Sensitivity Wet Fluorescent Magnetic Particle Testing (WFMT)
- Replication of surfaces
- Positive Material Identification (PMI)
- Thermographic temperature surveys

Summary

Hydrogen-related damage mechanisms are present in ammonia producing equipment. Having an understanding of these hydrogen damage mechanisms and how operations or process conditions can affect equipment will help mitigate the occurrence of hydrogen-related damage mechanisms. By making better distinctions between the three main hydrogen-related damage mechanisms, one will better identify and mitigate the damage mechanism.

The main hydrogen related damage mechanisms are:

High-Temperature Hydrogen Attack (HTHA)
Reaction of atomic hydrogen with carbides and formation of methane bubbles. It typically occurs above temperatures of 200°C (400°F).

Hydrogen Blistering, Hydrogen-Induced Cracking (HIC), Stress orientated Hydrogen-Induced Cracking (SOHIC)

Recombination of atomic-H to molecular-H2 at defects/segregations in the steel. It typically occurs in ‘dirty’ steels and with corrosion reactions generating atomic hydrogen.

Hydrogen Embrittlement

Atomic hydrogen hinders dislocation movement in the steel and causes brittle behavior. It typically occurs at temperatures below 150°C (300°F). This can also happen after cool-down when the steel has been charged with hydrogen during high-temperature service.

It is essential that these mechanisms be communicated to plant and management staff and that the preventative actions are implemented; otherwise, the high risks are not mitigated.

Acknowledgements

The shared information from the 2020 Joint Industry Program (JIP) facilitated by BakerRisk has contributed to the content of this paper. The JIP was a successful collaboration between a significant group of Ammonia producers to share materials and corrosion knowledge based on investigations after incidents.

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