WORLD FERTILIZER®

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Expertise-driven, experience-refined
Unleash Reliability from the lessons of yesterday!

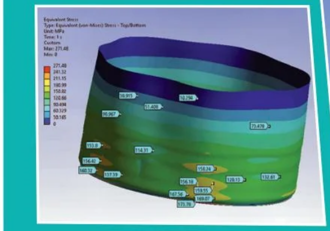
Fitness For Service (FFS)

Fitness for Service (FFS) assessments by TCR follow API 579, ASME FFS1, and BS 7910 standards. Our fracture mechanics methodology is globally recognized and applied across various industries including fertilizers & refineries.

FFS Assessment uses Analytical Methods to Evaluate Flaws, Damage, and Material Aging:

- Stress Analysis via Standard Handbook, Design Code Formulas, or Finite Element Analysis (FEA).
- Knowledge of past and forecast of future operating conditions.
- Non-Destructive Examination (NDE) to locate, size, and characterize flaws.
- Material Properties considering damage mechanisms, corrosion, and temperature effects.

The outcome of FFS study helps to take decision on Run, Alter, Repair, Monitor, or Replace the Equipment.



TCR ADVANCED

Optimizing Asset Integrity of Fertilizer Plant

India based, TCR Advanced Engineering specializes in providing in-depth consulting in the dynamic and ever-evolving fertilizer industry vertical. With an unparalleled depth of domain expertise, we empower our clients to optimize asset operations, maximize productivity, and achieve sustainable growth with full safety compliance. Since 1999, we have provided plant advisory services, metallurgical consulting and robotics-based NDT to QAFCO, SAFCO, OMIFCO, Chambal, Notore Chemical, Dangote, GSFC and others. We combine our technical proficiency with innovative solutions to deliver tailored strategies that enhance efficiency, determine remaining life and condition assessment of existing plant assets, streamline production processes, and ensure compliance with industry regulations. We understand the challenges of greenhouse gas emission and tailor our services offering in accordance with the local environmental standards.

RBI of Ammonia Storage Tanks

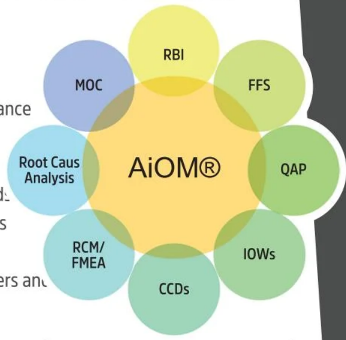
TCR Advanced's approach leverages RBI to optimize inspection and maintenance activities. By incorporating metallurgical knowledge into RBI technologies as per API580/581 assessments, we elevate the ability to assess and manage risks, ensuring the integrity and longevity of fertilizer plants.

Asset Integrity Optimization & Management (AiOM®)

Asset Integrity Optimization & Management (AiOM®) is a holistic approach that ensures the integrity of assets throughout their life cycle, from conception to retirement. It covers key elements such as people, system processes, and resources. Assets include equipment, tools, and instruments supporting plant operations. AiOM® utilizes various internationally recognized tools like Risk-Based Inspection (RBI), Fitness-For-Service (FFS), Reliability Centred Maintenance (RCM), Integrity Operating Windows (IOWs), and Quality Assurance (QA) Plans. These tools help optimize inspection and maintenance, minimize downtime, prevent losses, ensure compliance, mitigate risks, and enable efficient data preservation.

Advantages of AiOM®

- Expertise of Industry Veterans
- Damage Mechanism Identification
- Resource optimization for inspection and maintenance
- Reduced downtime and planned outages Loss prevention
- Compliance with regulations and industry standards
- Mitigation of health, safety, and environmental risks
- Proper documentation for future data retrievals
- Continuous monitoring of critical process parameters and emergency response Creation of a goal-oriented working environment.



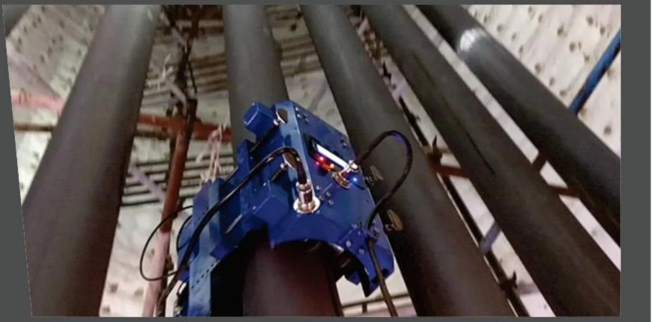
AiOM®
RBI
FFS
QAP
IOWs
CCDs
RCM/ FMEA
Root Caus Analysis
MOC

ARTiS - Reformer Tube Inspection

TCR has indigenously developed an automated robotic crawler to aid ultrasonic inspection of reformer tubes which provides tabular and interactive digital output. ARTiS can simultaneously collect tube data at an interval of 0.1m such as ultrasonic dB level of attenuation, the diameter of the tube and bowing angle at every location.

Following output will be provided:

- Remaining life of each reformer tube
- Summary table providing accumulated creep damage as on date of inspection
- Calculation on effective tube metal (skin) temperature
- Theoretical accumulated creep damage up to next shutdown
- Tube replacement when the accumulated creep damage exceeds 0.8 life fraction.



Optimize Your Assets, Empower Your Future

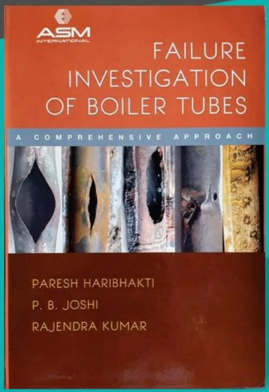
Scan the QR code now

and gain instant access to our cutting-edge White Paper on AiOM Tool - The Ultimate Solution for Efficient and Reliable Operations of Assets

Failure and Root Cause Analysis

TCR takes immense pride in its deep sectoral knowledge, gathering best practices from 6000+ failure investigations. These success stories include major projects in manufacturing and metallurgical failures on ASME boilers, pressure vessels, gas turbine engine components, oil and gas transmission pipelines, food processing equipment, heat exchangers, medical implants, aircraft/aerospace components, offshore structures, industrial machinery, weldments and ships.

Our recognition extends globally, with a book authored by our Technical Director, Mr. Paresh Haribhakti, published by ASM International, as well as a chapter in ASM Handbook – Volume # 11A.



ASM INTERNATIONAL
FAILURE INVESTIGATION OF BOILER TUBES
A COMPREHENSIVE APPROACH
PARESH HARIBHAKTI
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Mitigating the risk of HTHA

Paresh Haribhakti and Ketan Upadhayay, TCR Advanced Engineering, India, outlines how fertilizer producers can proactively detect high-temperature hydrogen attack (HTHA) to enhance plant safety.

Safeguarding industrial operations involving hydrogen is a critical concern, particularly in fertilizer production. The destructive impact of high-temperature hydrogen attack (HTHA) can lead to catastrophic brittle fractures in plant equipment without warning. Therefore, ensuring the integrity of equipment that is exposed to HTHA environments is of the utmost importance to prevent accidents and economic losses.

Traditional methods such as the advanced ultrasonic backscatter technique (AUBT) were effective, but required advanced skills for early detection of HTHA damage. While the renowned Nelson curves have addressed HTHA concerns, a tragic incident at the Tesoro Anacortes refinery in 2010, resulting in seven casualties, highlighted the need for a comprehensive solution beyond Nelson curves. To effectively mitigate HTHA damage, a risk-based assessment approach, combined with advanced non-destructive testing techniques such as high sensitivity wet fluorescent magnetic testing (HSWFMT) was required.

Time of flight deflection (TOFD), phase array ultrasonic testing (PAUT), full matrix capture/total focusing method (FMC/TFM), and in-situ metallography, have emerged enabling precise early detection of HTHA damage.

Unveiling HTHA: A key damage mechanism

It has been observed that the carbon and low-alloy steels used for piping, pressure vessels and heat exchangers exposed to high-temperature, high-pressure hydrogen service experience a loss of their strength and ductility, leading to catastrophic

brittle fracture. This type of damage is known as HTHA, or 'hydrogen attack'.[1] In ammonia plants, the most susceptible locations in which HTHA can occur are those near the ammonia converter outlet, high-temperature shift converter, the outlet nozzle of catalytic equipment, and the inlet nozzle of an exchanger, methanator, etc. The damage due to HTHA can occur at temperatures above 200°C and at hydrogen partial pressure of 0.80 MPa.[2]

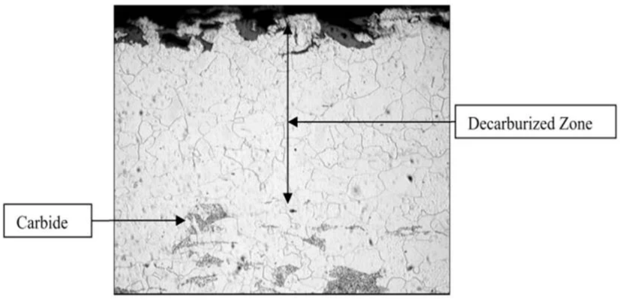

Figure 1. Optical micrograph showing internal decarburisation and the hydrogen induced fissures, at 200 x magnification.

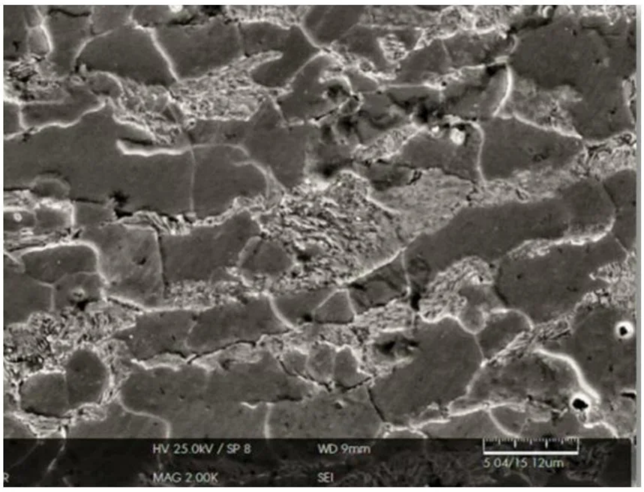

Figure 2a. SEM micrograph displaying the formation of voids along the grain boundaries of pearlite, indicating onset of HTHA.

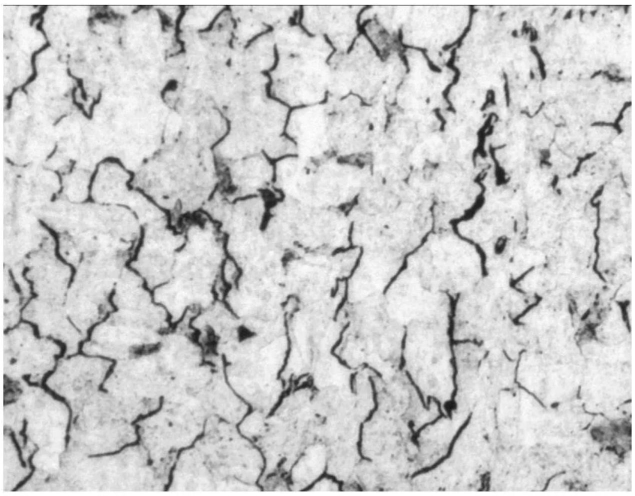

Figure 2b. SEM micrograph showing the final stage of formation fissures and micro-cracks.

At high temperatures, the molecular hydrogen thermally dissociates into atomic hydrogen (also known as nascent hydrogen). The root cause of HTHA is this atomic hydrogen that diffuses into the steel and reacts internally with the carbides (more precisely Fe_3C i.e., cementite for plain carbon steel, or M_3C i.e., alloy carbides for low-alloy steels) to produce methane (CH_4) bubbles along the grain boundaries or at non-metallic inclusions in the steel. As methane is insoluble in steel, it accumulates as gas bubbles in small pockets at grain boundaries and inclusions that are present in steel. Eventually, there is build-up of methane gas pressure to form cavities and fissures within the steel that ultimately unite to form cracks.

The characteristic feature of HTHA damage is hydrogen-induced decarburisation at the surface and/or in the interior of the part, and fissuring and/or cracking at grain boundaries of steel. The surface decarburisation accounts for a drop in the surface hardness of the steel, whereas the internal decarburisation can lead to formation of fissures, blisters or cracks. The fissuring results in a significant and permanent drop in ductility of the steel. The extent of damage can be assessed by optical microscopy and advanced NDE techniques. Figure 1 is an optical micrograph showing internal decarburisation and the hydrogen induced fissures in steel. HTHA damage occurs in four stages, namely the incubation period, followed by the second and third stages of surface and internal decarburisation causing partial deterioration of mechanical properties and the final stage of fissuring and cracking. Figure 2a represents onset of HTHA, whereas Figure 2b corresponds to fissuring and cracking.

Failures due to HTHA have mainly been reported in the case of plain carbon steels and low-alloy steels. Welds of carbon steel equipment and pipelines, either with post-weld heat treatment (PWHT) or without PWHT are susceptible to failure due to HTHA. Likewise, low alloy steels of the type C-Mo, Cr-Mo and Cr-Mo-V are also prone to HTHA.[3] The carbide stabilising elements such as chromium, molybdenum, vanadium and niobium in low-alloy steels offer improved resistance to HTHA compared to carbon steels due to greater stability of their carbides compared to cementite.

Ammonia process technology and the potential of HTHA

Ammonia is one of the most frequently used global chemical products in the production of nitrogen-rich agricultural fertilizers such as urea, ammonium nitrate, diammonium phosphate (DAP) and mono-ammonium phosphate (MAP).

The hydrogen required for ammonia synthesis in the Haber-Bosch process[4] is produced by reacting methane (natural gas) with steam in the presence of a nickel catalyst at 770°C in the primary reformer, and in the presence of air at 735°C in the secondary reformer, respectively followed by removal of water, carbon monoxide and carbon dioxide in shift converters. The nitrogen from air is then mixed with hydrogen and the resultant gas mixture is compressed to 20 – 30 MPa pressure and fed to the ammonia synthesis reactor in the presence of the iron catalyst to form ammonia. With the advancements in science and technology and further understanding of the Haber-Bosch process, new processes/technologies of the ammonia synthesis have been evolved. Some of the new processes/technologies for ammonia synthesis area include:[5]

- The MWK or Kellogg process.
- The KBR or Kellogg Brown & Root process.
- The Haldor Topsoe process.
- TKIS or thyssenKrupp Industrial Solutions' processes.
- The LAC or Linde Ammonia Concept process.
- Udhe Krupp's processes.
- Toyo Engineering and Casale's technologies.

Since steels are liable to HTHA normally above a temperature of 200°C, all the above processes that employ different grades of steel for equipment and pipelines have a potential threat as far as damage due to HTHA is concerned.

Basis of evaluation of HTHA damage

To effectively mitigate the risk of HTHA in the fertilizer industry, a thorough evaluation of various factors is necessary. These factors include the material of construction (MOC) of equipment, operating temperature, partial pressure of hydrogen, and exposure time. The evaluation should also consider the presence of carbide-stabilising alloying elements in low-alloy steels, such as chromium, molybdenum, vanadium, and niobium, which offer greater resistance to HTHA compared to plain carbon steels.

The evaluation process begins with understanding the properties and behaviour of the MOC under hydrogen exposure. This includes examining the composition, microstructure, and mechanical properties of the material. Grain size, impurities, and the stability of carbides are also important factors that influence the material's susceptibility to HTHA.

Operating temperature plays a critical role in HTHA risk assessment. High temperatures accelerate the diffusion of hydrogen into the material, increasing the likelihood of damage. The evaluation should determine the maximum allowable temperature for the MOC based on its HTHA resistance and the specific process conditions.

The partial pressure of hydrogen in the operating environment is another significant factor. Higher hydrogen partial pressures increase the potential for hydrogen absorption and subsequent HTHA. The evaluation should establish safe limits for hydrogen partial pressure, considering the material's HTHA resistance and the process requirements.

Exposure time is an essential consideration in evaluating the risk of HTHA. Prolonged exposure to hydrogen at elevated temperatures can lead to cumulative damage. Therefore, the evaluation should assess the expected service life of the equipment, and consider the time-dependent nature of HTHA.

In addition to these primary factors, the evaluation may also consider secondary factors that influence HTHA susceptibility. These can include the presence of residual or operating stresses, the type of weld (with or without PHWT), and the level of impurities in the material.

To support the evaluation process, empirical data, field experience, and industry standards such as API Recommended Practice (RP) 941 and API RP 581 can provide valuable guidance. These resources provide information on material performance, operating limits, and inspection guidelines based on historical data and research.

Nelson curve for HTHA assessment

American Petroleum Institute (API) Recommended Practice (RP) 941,[6] entitled 'Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants' is an industrial standard (which uses graphical representation/curves known as Nelson curves), that has been followed over the years to help decide the suitability of a material for hydrogen service. Nelson curves are the plots of partial pressure of hydrogen vs operating temperature to which a steel is exposed, and predict the conditions in which HTHA can occur/will not occur for different steels (Figure 3). Operating conditions that fall above the curve point towards the risk of HTHA, whereas Figure 3 indicates the situations where the damage due to HTHA is unlikely. Nelson curves define the operating limits to avoid decarburisation and fissuring of steel in hydrogen service. However, of late it has been realised that risk of damage due to HTHA cannot be solely judged on the basis of Nelson curves because of several limitations:

- The Nelson curve does not take into account time in service.
- Damage due to HTHA also depends on factors such as grain size, level of impurities, stability of carbides, type of weld (i.e., with or without PHWT), and acting or residual stress. These factors are not taken into consideration by the Nelson curves.

- Nelson curves are subject to revision from time to time. History says that based on experience, the curves for carbon and C-1/2 Mo steels are lowered with respect to temperature scale.
- Most of the data used in developing earlier curves is based on steels in annealed condition. This does not apply to normalised or quenched and tempered steels.

Inspection methodology for HTHA

Traditionally, AUBT is used for detection of damage due to HTHA. It is used as a screening tool to identify the presence of micro-cracks in parent material. However, it has limited data recording capability and is highly dependent upon technicians' skill.

Some of the modern inspection techniques used for detecting damage due to HTHA[7] are:

- High sensitivity wet fluorescent magnetic testing (HSWFMT).
- Time of flight diffraction (TOFD).
- Phased array ultrasonic testing (PAUT).
- Full matrix capture/total focusing methods (FMC/TFM).

Among the non-ultrasonic techniques, HSWFMT is used especially for non-PWHT carbon steels where cracking is most likely related to welds.

TOFD is a preferred method for inspection of HTHA related damage of welds and heat affected zones. In a TOFD system, transmitter and receiver probes are placed on opposite sides of a weld. The longitudinal sound waves passed between the probes detect, locate, and estimate the size of the flaws based on the time of flight of any diffracted beam. TOFD calculates the response time of low-amplitude waves that are diffracted by the tips of discontinuities.

Instead of a single transducer and beam, the PAUT technique uses specialised multi-element 'array' transducers. This technique uses programmed piezoelectric elements that pulse individually at calculated time intervals, along with angled ultrasonic beams, to provide 3D images that can unveil difficult-to-detect cracks or flaws. It is used to detect clusters of methane voids and micro-fissures.

The FMC method uses standard phased-array ultrasonic probes to acquire data from every possible pulse-receive element (typically 16 to 64) combination of the probe array. The data captured by FMC is post-processed using a signal processing routine such as TFM that reconstructs the information to produce high-resolution two-and three-dimensional images for interpretation purposes. The combination allows for higher detection of small defects, such as those in the early stage of HTHA.

Some of the shortcomings of empirical Nelson curves were addressed by API RP 581, Risk-Based Inspection Technology, Third Edition (2016)[8], which provides quantitative risk-based inspection (RBI) methods. Based on the recommendations of API 581, a more stringent set of conditions are laid down that permit the use of components affected by HTHA.

These include past history of HTHA damage during service, MOC of the component, upper limit of operating temperature, hydrogen partial pressure, manufacturing method, PWHT, etc. It is possible to identify the risk involved in hydrogen service as offline study, and depending on the risk assessment, inspection guidelines can be framed with the help of metallurgical experts that have experience in the field of HTHA.

Conclusion

Mitigating the risk of HTHA in the fertilizer industry requires a systematic approach that includes evaluation, risk assessment, inspection, and defining the operating window. By evaluating factors such as MOC, operating temperature, hydrogen partial pressure, and exposure time, plants can identify equipment and processes that are susceptible to HTHA. Utilising advanced inspection techniques, such as HSWFMT, TOFD, PAUT, and FMC/TFM, enhances the detection capabilities for early-stage HTHA. Defining the operating window establishes specific limits to ensure safe operation and minimise the risk of HTHA-related failures. By implementing these strategies, the fertilizer industry can effectively mitigate the risk of HTHA and ensure the safety and reliability of their operations. **WF**

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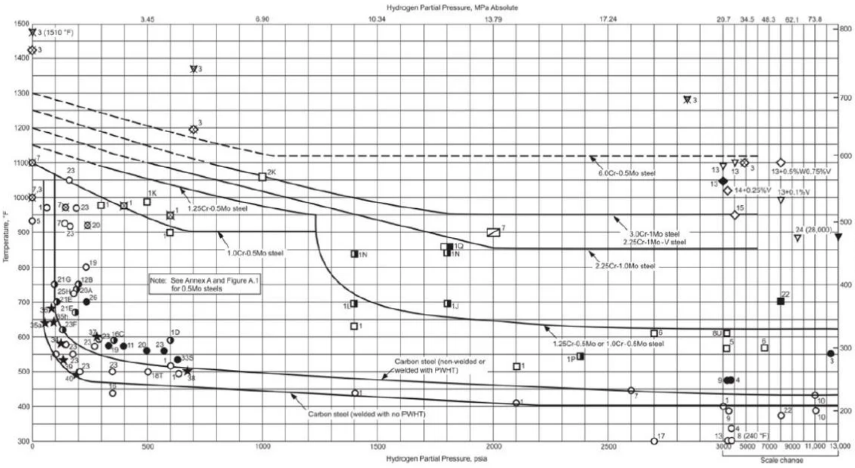

Figure 3. Operating limits for steels in hydrogen service to avoid HTHA.[6]