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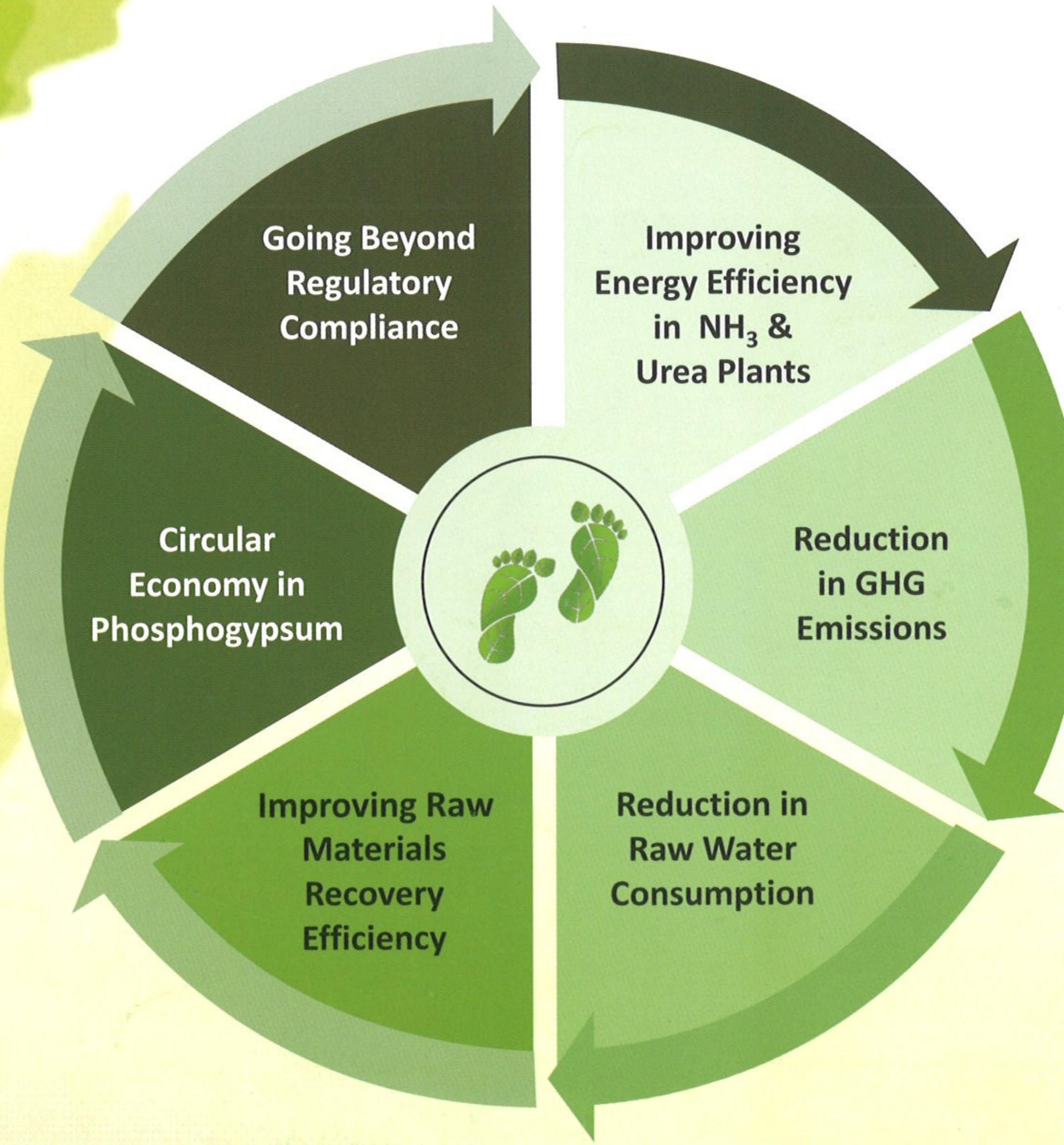

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An Early Detection of HTHA – A Key to Safe Plant Operation

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Abstract

Steels operating at elevated temperature in hydrogen environment are prone to degradation by a mechanism known as high temperature hydrogen attack (HTHA). It is an insidious type of attack that occurs in process equipment and piping exposed to hydrogen at elevated temperatures (> 200 °C), under dry conditions. Material degradation due to HTHA can result in sudden and catastrophic brittle failure. It is, therefore, necessary to monitor the integrity of equipment in HTHA-service so as to avoid accidents. Traditionally, Nelson curves have been used to decide the safe operating limits for steels in hydrogen service to avoid HTHA but have their own limitations. Advanced ultrasonic backscatter technique (AUBT) has been used to carry out on-going inspection for HTHA, but it requires significant expertise. Hence, techniques like wet fluorescent magnetic testing (HSWFMT), time of flight deflection (TOFD), phase array ultrasonic testing (PAUT), and full matrix capture/total focusing method (FMC/TFM) have been developed for early detection of damage due to HTHA.

Key words : High temperature hydrogen attack, high temperature corrosion, HTHA inspection techniques, early detection of HTHA

Introduction

High-temperature hydrogen attack has been a threat to industries dealing with hydrogen, including fertilizer industry for many years. The damage due to HTHA leads to disastrous situation in view of the catastrophic nature of brittle fracture of the affected plant equipment without any warning. Hence, monitoring the integrity of equipment subjected to HTHA environment is of utmost importance so as to avoid accidents and economic losses. In good old days, failures due to HTHA were detected using technique known as AUBT. This technique provided reasonable results, but required higher level of skill for early detection of onset of HTHA damage. The issue of HTHA has also been addressed by famous Nelson curves which provide the stability limits for various steels as a function of temperature and hydrogen partial pressure. However, the incident of explosion in the heat exchanger at Tesoro Anacortes refinery in the year 2010 with seven casualties, warned about the damage potential of the HTHA if it goes unchecked and showed that the Nelson curves alone cannot be the ultimate solution to HTHA problem.

Apart from operating temperature and the hydrogen partial pressure, HTHA is also governed by several factors like thermodynamics, metallurgical parameters and manufacturing methods. Hence, the risk-based assessment of equipment used in HTHA susceptible environment is a present day need so as to avoid failures. With the advancements in nondestructive testing techniques like HSWFMT, TOFD, PAUT, and FMC/TFM along with *in-situ* metallography; early detection of HTHA damage has become possible with higher precision. A multi-fold approach like risk- based assessment along with use of NDT techniques can help in mitigating HTHA damage.

About HTHA

Equipment of ammonia plant in a fertilizer complex suffer from various high temperature attacks such as the oxidation, nitriding, metal dusting, HTHA, stress relaxation cracking and creep of which, the HTHA is the most important damage mechanism.

It has been realized 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 a catastrophic brittle fracture. This type of damage is known as HTHA, or 'hydrogen attack' (Viswanathan, 1989). The weld and its nearby location such as the heat affected zone (HAZ) are the preferred sites for HTHA to take place. The damage due to HTHA can occur at temperatures above 200 °C and at hydrogen partial pressure of 0.80 MPa or so (Ureaknowhow.com, 2020).

At high temperature, 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

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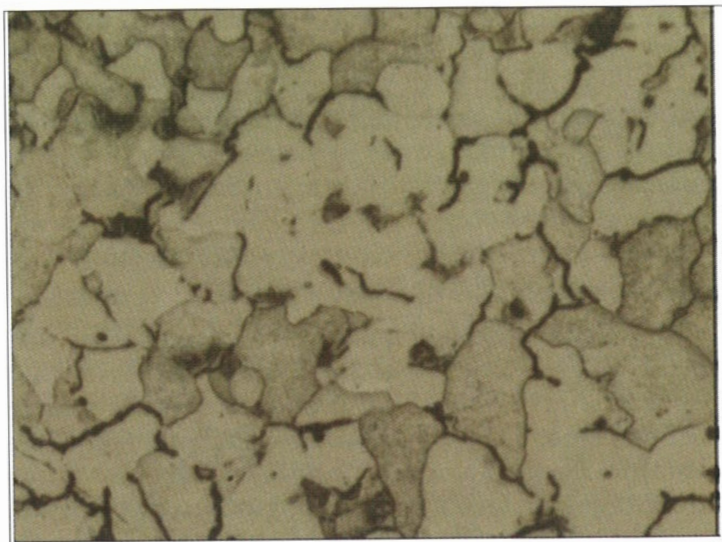

Photo 1a. Optical micrograph showing internal decarburization and the hydrogen induced fissures

Photo 1b. SEM micrograph displaying formation of voids along the grain boundaries of pearlite indicating onset of HTHA damage.

or M_3C *i.e.* alloy carbides for low-alloy steels) to produce methane (CH_4) bubbles along the grain boundaries or at nonmetallic inclusions in the steel. The diffusivity of atomic hydrogen in steel is a function of partial pressure of hydrogen, the operating temperature and exposure time. Longer the time of exposure of the steel at operating temperature and hydrogen partial pressure above the safe working limit, the more will be the extent of damage. Methane being insoluble in steel, accumulates as gas bubbles in small pockets at grain boundaries and inclusions 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. Alternatively, the atomic hydrogen can recombine to form molecular hydrogen leading to similar effects as that of methane.

The characteristic feature of HTHA damage is hydrogen induced decarburization at the surface and/or in the interior of the part and fissuring at grain boundaries of steel. The internal decarburization can cause fissures along the grain boundaries of the steel or lead to formation of blisters on the surface of stringer type inclusions such as that of MnS. The fissuring results in significant and permanent drop in ductility of the steel. **Photo 1a** is an optical micrograph showing internal decarburization and the hydrogen induced fissures in steel whereas **Photo 1b** is a SEM micrograph that shows the onset of damage by way of formation of perforations/voids along the grain boundaries of pearlite in the steel subjected to HTHA. These voids eventually unite to form micro-cracks along the grain boundaries of the steel.

The damage due to HTHA does not initiate as soon as the equipment is exposed to temperature in excess of so called critical temperature. There is a period of time, known as incubation time, during which there is no significant change in the properties of the steel. In the initial stages of attack known as incubation period, the damage is so microscopic that it cannot be detected by current nondestructive examination (NDE) and metallographic methods. During the second and third stage of HTHA either surface decarburization or internal decarburization occurs. Of which, the surface decarburisation accounts for drop in the surface hardness of the steel and is usually not a matter of concern. However, the internal decarburization as a result of formation and entrapment of methane can lead to permanent damage in the form of fissures, blisters or cracks. The extent of damage can be assessed by optical microscopy and advanced NDE techniques. A deterioration in the mechanical properties of the steel is observed. When the pressure exerted by entrapped methane gas molecules exceeds the strength of the steel, permanent damage occurs. The fourth stage (the final stage) is the one where carbon in solid solution is reduced to compromise material's mechanical properties to a level where cracking can occur.

Failures due to HTHA have been reported mainly in 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 subject to HTHA (Nelson, 1949). However, it is noteworthy that carbide stabilizing alloying elements like chromium, molybdenum, vanadium and niobium used in low alloy steels offer greater resistance to HTHA compared to carbon steels in view of the greater stability of their carbides compared to cementite and thereby lesser tendency to methane formation. Higher the alloy content of a low-alloy steel, the critical exposure temperature makes a steel susceptible to increase in HTHA.

Ammonia Process Technology and Potential of HTHA

Ammonia is one of the largest global chemical products that is used in the production of nitrogen-rich agricultural fertilizers such as urea, ammonium nitrate, diammonium phosphate and mono-ammonium phosphate. About 80% of total world production of ammonia is used in the manufacture of fertilizers with global production of about 183 million MT in 2019. The hydrogen required for ammonia synthesis in Haber-Bosch process is produced by reacting methane (natural gas) with steam in the presence of nickel catalyst at 770 °C in primary reformer and in the presence of air at 735 °C in secondary reformer, followed by removal of water, carbon monoxide and carbon dioxide in shift converters. Traces of CO and CO_2 in the syngas are further removed by converting them to methane and water in a methanator in the presence of Ni/Al_2O_3 catalyst at approximately 325 °C temperature before it enters the ammonia converter. The nitrogen is drawn from air during secondary reforming. Thus, hydrogen and nitrogen obtained after purification is compressed to 15 to 30 MPa pressure and fed to ammonia synthesis reactor in the presence of iron catalyst to form ammonia. The ammonia synthesis reaction is exothermic and can be expressed as:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92.28 \text{ kJ mole}^{-1}$$

The ammonia is condensed to a temperature of 5 °C and is separated in a pressure separator. The unreacted hydrogen and nitrogen are then recycled back and mixed together with the new feedstock. **Figure 1** gives the block diagramme of ammonia synthesis using Haber-Bosch process.

With the advancements in science and technology and further understanding of the Haber's process, new processes/technologies of ammonia synthesis have been evolved. Though, the basic underlying principle remains the same, these modern processes offer advantages in terms of improvements in catalysts used in reformers; methanation and ammonia synthesis; modification in plant layout from multi-train to single train; enhanced heat recovery; and in turn greater energy efficiency; improved process control and safety, and so on.

Since, the steels are prone to HTHA normally above a temperature of 200 °C, all the above processes employing different grades of steel as equipment and pipelines, have a potential threat as far as the damage due to HTHA is concerned. In ammonia plant, the most susceptible locations where HTHA can occur are those near ammonia converter outlet, high temperature shift converter, the outlet nozzle of catalytic equipment, and the inlet nozzle of an exchanger, methanator, etc.

Role of Nelson Curves in HTHA

American Petroleum Institute (API) Recommended

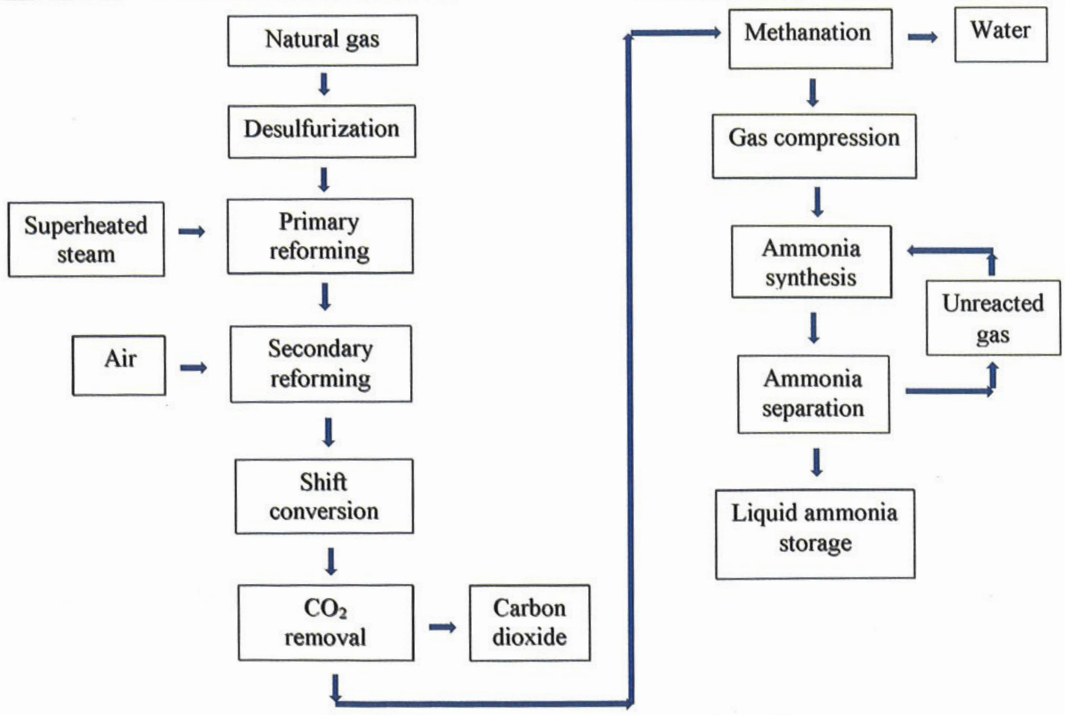

Figure 1. Block diagramme of ammonia synthesis by Haber-Bosch process

Practice (RP) 941 (American Petroleum Institute, 2016), 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, has been followed over the years for deciding the suitability of a material for hydrogen service. Nelson curves, were developed by G. A. Nelson way back in 1949, on the basis of data compiled for observed performance of a steel exposed to hydrogen environment at elevated temperature. The curves are revised/updated from time to time as and when there is generation of new empirical data. 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. Those operating conditions which fall above the curve point towards the risk of HTHA whereas the one below the curve indicate the situations where the damage due to HTHA is unlikely. In other words, if a equipment or pipeline is subjected to service at temperature and partial pressure of hydrogen which fall above the Nelson curve, then its material of construction (MOC) is not suitable for service under those set of conditions and is susceptible to HTHA. A typical Nelson curve giving operating limits for steels in hydrogen service so as to avoid HTHA is shown in **Figure 2.**

The dashed portion of the curve (which corresponds to high temperature-low pressure condition) indicates the tendency of the steel to surface decarburization whereas the solid lines (low temperature-high pressure condition) indicate the tendency to internal attack in the form of fissures and cracks. At high temperatures and high hydrogen partial pressures, both mechanisms are active. In short, Nelson curves define the operating limits to avoid decarburization and fissuring of steel in hydrogen service. However, it has been realized that risk of damage due to HTHA cannot be solely judged on the basis of Nelson curves because of several limitations of Nelson curves such as:

- Nelson curve approach takes no account of the time in service.
- Nelson curves are not only governed by variables like operating temperature, partial pressure of hydrogen and the MOC of the steel but also depend on factors like grain size, level of impurities, stability of carbides, type of weld (*i.e.* with or without post weld heat treatment), acting or residual stress, etc. to name a few. These factors are not taken into consideration by the Nelson curves. For example, earlier the effect of PWHT of steels on resistance to HTHA was not well understood. It is realized that PWHT of welded or non-welded steels offers increased resistance to HTHA.
- Nelson curves are subject to revision from time to

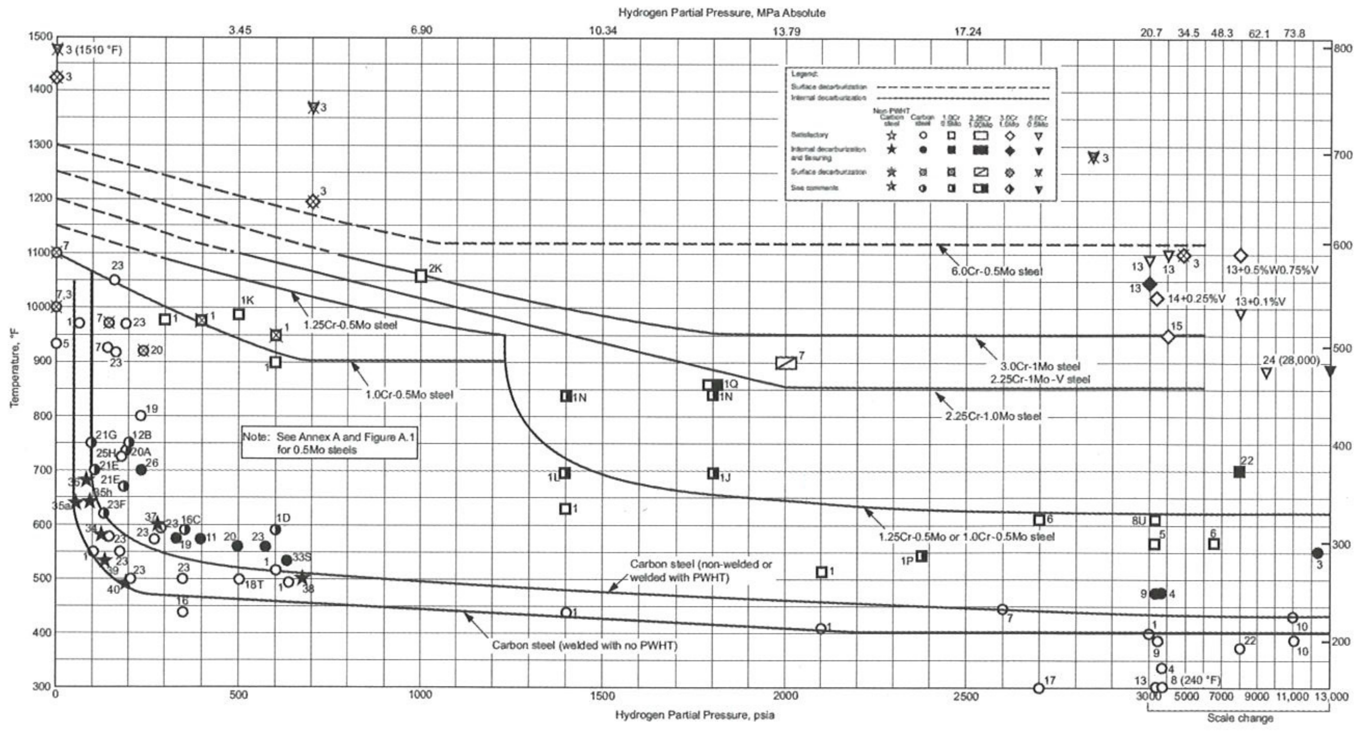

Figure 2. Operating limits for steels in hydrogen service to avoid HTHA (Source : American Petroleum Institute, 2016)

time. Past history says that based on the field 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 and does not apply to normalized or quenched and tempered steels.

Inspection Methodology for HTHA

Early stages of HTHA are very difficult to detect, because of the small size of the methane voids (typically <0.1 mm) which is much smaller than the wavelength of ultrasound employed for detection of micro-defects like, fissure, voids and micro-cracks. Traditionally, AUBT is used for detection of damage due to HTHA. Ultrasonic waves backscattered from within the metal are used to evaluate subsurface microstructural features/defects and the depth of region affected. 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 technician's skill.

Some of the modern inspection techniques used for detecting damage due to HTHA (Channa Nageswaran, 2018) are :

- High sensitivity wet fluorescent magnetic testing (HSWFMT)
- Time of flight deflection (TOFD)
- Phase array ultrasonic testing (PAUT) and
- Full matrix capture/total focusing method (FMC/TFM)

Among the non-ultrasonic techniques, HSWFMT has recently gained considerable attention. The technique is used especially for non-PWHT carbon steels where cracking is most likely related to welds. TOFD has been a preferred method for inspection of HTHA related damage of welds and heat affected zones. It offers rapid screening of large areas with a high probability of detection (PoD). In a TOFD system, ultrasonic probes (transmitter and receiver probe) 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. Increased gain noise (short indications) and clustering are indicative for early stage HTHA.

The other testing *i.e.* PAUT has been recognized as one of the best techniques for HTHA inspection. The PAUT is based on the use of specialized multi-element "array" transducers. Instead of a single transducer and beam, the 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. Simultaneous use of phased array UT and TOFD can detect all types of welding flaws.

In addition to above, FMC/TFM is a relatively new phased-array technology that utilizes signal measurement and processing algorithms for better detection and measurement capabilities for weld flaws in HTHA.

FMC uses standard phased-array ultrasonic probes to acquire data from every possible pulse-receive element (typically 16 to 64) combination of the probe array. FMC captures and records A- scan signals from in sequence pulsed and receiving elements in the 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 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) (American Petroleum Institute, 2019 & 2020). It is the recommended practice developed and published by API to provide quantitative risk-based inspection (RBI) methods. RBI is a methodology that involves quantitative assessment of the probability of failure and the consequence of failure associated with each equipment/item in a particular process unit. According to API 581, the RBI programme has four major goals:

- Identify and measure the risk for all covered equipment,
- Impart an accurate understanding of risks and risk drivers,
- Enable effective risk management and
- Reduce risks associated with operating processing facilities.

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. Each one has an influence on the performance of the component. 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 having experience in the field of HTHA.

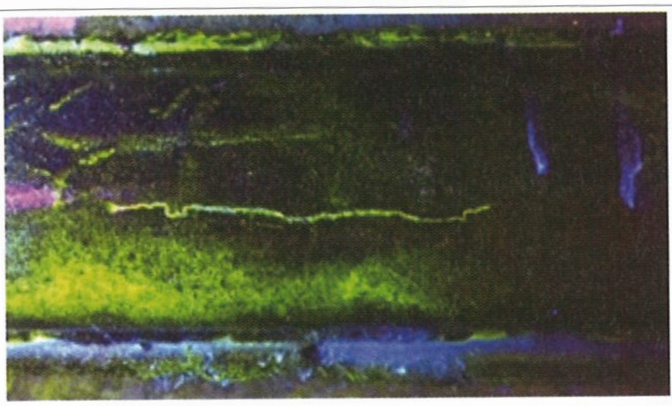

Photo 2. Photograph of the header sample in WFMPI tested condition showing linear indication

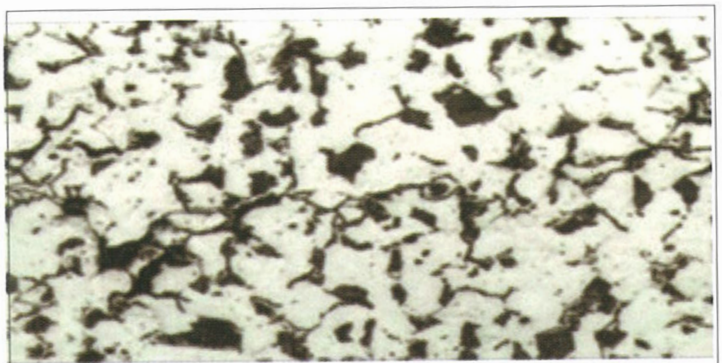

Photo 3a. Microstructure showing grains of ferrite and pearlite besides the signs of internal decarburization, grain boundary fissures and micro-cracks

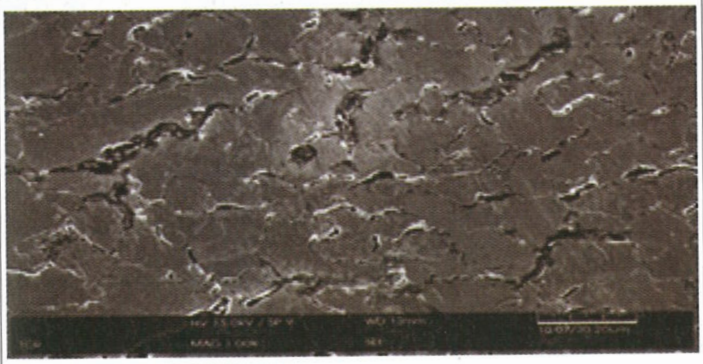

Photo 3b. SEM image showing fissures and micro-cracks

Case Study

Leakage of high-pressure process gas was detected from a transfer line of 1250 TPD ammonia plant in a fertilizer complex after 12 years of service. The pipeline was made up of C-0.5Mo steel. The operating temperature was about 400 °C and the partial pressure of the gas was 2.5 MPa. The dimensions of the transfer line pipe were 150 mm diameter x 14 mm wall thickness. The failed sample was subjected to visual examination followed by wet fluorescent magnetic particle inspection (WFMPI). Linear indications were observed as shown in **Photo 2**.

The failed sample was subjected to AUBT using GE Krautkramer USM-36, ultrasonic flaw detector by which the presence of internal fissures and damage could be identified. The AUBT results indicated typical pattern for internal fissures in the material with back scatter as well as the high attenuation. The low-magnification examination using stereo microscope revealed the presence of a discontinuous hairline crack. The microstructural examination indicated damage due to HTHA by way of internal decarburization, formation of grain boundary fissures and microcracks **Photo 3a**. The SEM after metallography further confirmed the grain boundary fissures and intergranular cracking as shown in **Photo 3b**.

Based on the findings of this investigation, the failure was attributed to HTHA.

Conclusion

Failures are reported in the ammonia plant despite of adherence to safety guidelines and periodic inspection. Inspection for HTHA is a challenging task requiring significant expertise. As the plant becomes older, many equipment and utilities get affected and lead to failures due to various damage mechanisms including HTHA. Timely inspection and risk assessment is the key to safe and hazardless operation of plant and equipment of ammonia plant.

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