API RP 586 Inspections for HTHA and API 941 Remaining Life Prediction Methodologies[1]

Unlike previous API documents, API's new RP 586 Section 2 provides guidance for the use of optimized inspection techniques for high temperature hydrogen attack (HTHA). Most of these are volumetric Ultrasonic Testing (UT) methods and were not previously included in API RP 941. Useful discussions of inspection limitations are included in this paper. With these new methods, Fitness-for-Service (FFS) assessments can now be conducted with much higher confidence. Several commercial models and an overarching FFS module that is being developed for Carbon Steel and Carbon ½ Moly are presented, as well as some of the new guidance in the forthcoming revision of API 941.

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Introduction

The purpose of this paper is to provide some background, perspective and a forward looking view to some ongoing and future evolutions of Mechanical Integrity development in Non-Destructive Evaluation (NDE) and Fitness For Service (FFS) advancement for assessment of High Temperature Hydrogen Attack (HTHA) as it relates to the Ammonia Industry. A brief summary of the mechanism, historical challenges, and the current and ongoing efforts to better identify, define and manage Carbon steel (and Carbon - ½ Moly) equipment that may be subjected to HTHA in service is included. The focus of this paper is to present a summary of American Petroleum Institute (API) soon to be released Recommended Practice (RP) 586, *NDT Methods for Equipment Damage Mechanisms*, Section 2 that provides guidance for the use of optimized inspection techniques (most volumetric Ultrasonic Testing (UT) methods are not found in previous API RP's) as well as useful discussions of limitations. With the promulgation of these new NDE methods, FFS assessments can be conducted with much higher confidence than previously possible. A few commercial models are available and the effort for an overarching FFS module is under development for Carbon Steel and Carbon - ½ Moly steel. In addition, the forthcoming revision of API 941 will be significantly different in the guidance provided (but existing API RP 941 Eighth Edition curves are expected to remain the same as in the previous edition) for material selection criteria based on a time-based service curve, not just a temperature and hydrogen partial pressure curve.

HTHA Background

HTHA has been an issue in pressure vessels and piping for many years. [1] The industrial origins can be traced back to the ammonia synthesis industry when Haber developed a process for "synthesis ammonia from the elements" around 1905.

1 67th Annual AICHE Safety in Ammonia Plants & Related Facilities

That ammonia synthesis could not be used commercially, as there were no vessels that would prevent hydrogen from flowing through yet withstand the elevated temperatures and pressure required. The company Haber worked for at the time had a technician, Carl Bosch, who was responsible for implementing this technology. After several conventional Carbon steel vessels exploded, Haber found that the hydrogen could penetrate Carbon-free iron without damage at these temperatures. Bosch solved the problem by inserting a liner of low-Carbon, soft iron, which allowed the penetrating hydrogen to escape through holes (Bosch Holes) in the pressure-bearing steel jacket, as shown in Figure 1. [2]

The development of Cr-Mo-steels had greatly expanded the safe operation range for high temperature high pressure hydrogen but Carbon steel and Carbon - ½ Moly (C-0.5 Mo) steels were still widely used in piping and vessels. Therefore, guidelines were established that were later adopted by the American Petroleum Institute (API) in their Recommended Practice (RP) for *Steels for Hydrogen Service at Elevated Temperatures and Pressure in Petroleum Refineries and Petrochemical Plants*. API Recommended Practice. [3] Originally compiled by G.A. Nelson, this practice became known as the "Nelson Curves" and has served the industry well albeit with many modifications. As it is essentially a summary of empirical data, it has been revised numerous times over the seven decades of its use. In the late 1970s, operational experience with C-0.5Mo had led the industry to consider "lowering" and later removing the C-0.5Mo curve. A good history of the evolution of this practice can be found in literature sources. [4]

HTHA Mechanism

HTHA has been a longstanding problem in the Oil Refining Industry. The Nelson Curves, which delineate temperature-pressure limits below which no attack occurs for long exposures, are listed in a chart. Applying Nelson Curves provides a go/no-go basis of selecting steels for hydrogen service; however, the curves provide no quantitative indication of the time required to produce an attack, nor a corresponding level of degradation of mechanical properties when the temperature-pressure limits are exceeded.

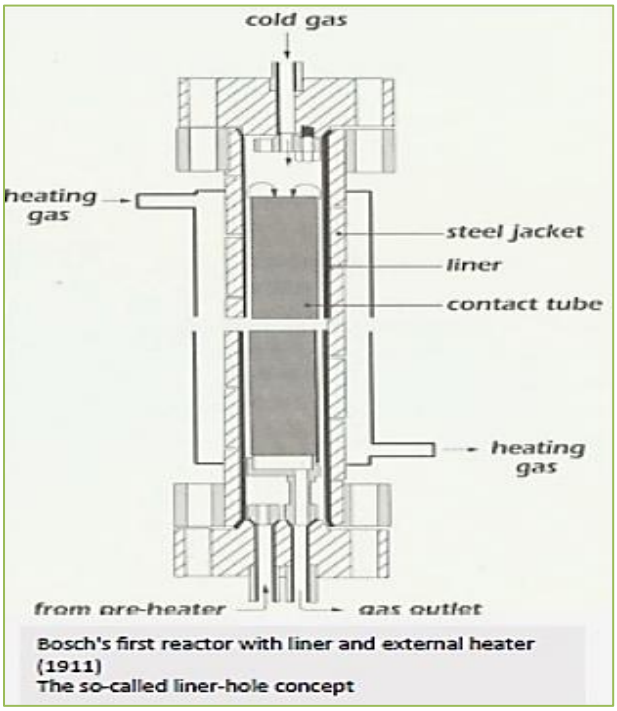

Figure 1. Early vintage Ammonia Synthesis reactor with "Bosch Holes." [2]

HTHA can be described as a loss of strength and ductility that can occur in steel exposed to hydrogen at high pressure and elevated temperature. This damage is attributed to the diffusion of atomic hydrogen into the steel. The reaction between the hydrogen and the iron-carbide in the steel forms methane, internally, at grain boundaries. The overall process of attack may be expressed by the equation:

$Fe_3C + 2H_2 (gas) = 3Fe + CH_4 (gas)$

Since methane is a larger molecule than hydrogen, it cannot diffuse out of the metal. Thus, the methane accumulates at the boundaries and may develop pressure, causing cracking along those boundaries.

Steel exposed to hydrogen attack conditions will pass through an incubation period before an actual attack is initiated. During the incubation period, steel that has absorbed hydrogen may suffer a slight loss in ductility and fracture toughness. While undergoing this incubation exposure, no visible macroscopic or low magnification microscopic changes in structure, composition, or physical properties can be detected. Following incubation, advances of HTHA are often, but not always, characterized by decarburization and formation of methane as shown in Figures 2 and 3. Further attack produces more decarburization, fissuring at grain boundaries and eventual crack formation in the structure. [5]

Figure 2: A pipe ID surface exhibiting complete decarburization of the original structure, magnified at 200X. [5]

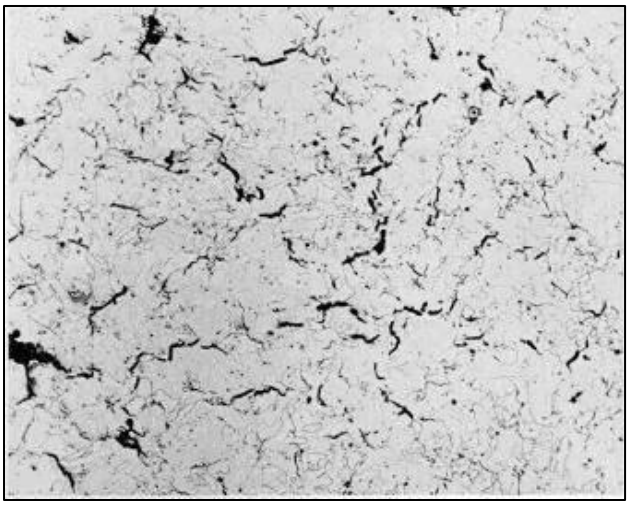

Figure 3: High magnification photomicrograph showing linkup of micro fissures to form continuous cracks and damage is accompanied by a significant amount of decarburization (~500 X) [5]

2010 HTHA Incident Significantly Transformed Needs for Better NDE and Modeling of HTHA

As described in the evolution of the Nelson Curves, incidents of failures involving HTHA in steels continued to be reported by the ammonia and petrochemical plants even when components were operated below their referenced Nelson Curves. [4] An incident involving multiple fatalities occurred in 2010 at Tesoro Refining (Anacortes, Washington), following a sudden and catastrophic failure of a Carbon steel component heat exchanger that produced a fire, resulting in seven fatalities. The Naphtha Hydrotreater heat exchanger at Tesoro had reportedly operated within the guidelines suggested by the API RP 941, and based on API RP 941 (2008), the damage on Tesoro Refinery vessel should not have occurred. The vessel had been evaluated for risks and additionally, according to the existing NDE techniques of the time (historic) both pre and post incident. Thus, that failure and other reported failures of Carbon steel components (both Post Weld Heat Treated (PWHT) and non-PWHT operating below the Nelson Curve have prompted engineers and designers to address the current

position of Carbon steel curves in API 941. [6] Following its investigation of the Tesoro incident, the Chemical Safety Board (CSB) recommended against using the Carbon steel component above a hydrogen partial pressure of 50 psia (3.4 bara) and temperature of 400°F (204°C).

In 2012, a Joint Industry Project (JIP) was launched consisting of support from eight petrochemical companies (ranging from multi-national integrated oil companies to single site refineries) to conduct evaluations of out-of-service HTHA damaged samples. The samples were collected and evaluated by different service providers under identical conditions, using similar NDE methods. This test bed of samples included the failed and similar serviced exchanger from the 2010 incident and provided a basis for evaluations using newer NDE methods.

Also at this time, advances in UT transducer manufacturing, signal processing and the computing speed and memory of field test equipment produced more powerful UT resources for this type of inspection, interrogation, and storage. [7]

Relevant Ammonia Equipment HTHA Cracking

Not only was the original notable occurrence of HTHA found in ammonia synthesis equipment, but there have also been historical instances of HTHA in ammonia plants recorded in both API documentation and other sources.

Failure of ammonia plant equipment due to HTHA can occur, especially if an attack happens and is not discovered for some time. Often times, the material compromised by HTHA may fail on startup, shutdown or during offline maintenance. Equipment such as methanators, shift equipment, and equipment near the ammonia converter and synloop have had HTHA cracking identified. The following is a brief summary from the API 941 TR document and other sources. [8] Points 32, 48 and 53 were used in the Nelson Curve plots.

Point 32. Ammonia Plant, very little additional information was reported other than the following: Normal temperature to condenser 400°F (204°C), hydrogen partial pressure 4000 psi (276 bar). Bypassing in converter increased temperature to about 480°F (249°C) to the water box type condenser during the last year of operation. Harp connector tube ruptured. Severe decarburization and fissuring occurred.

Point 48. Ammonia Plant Converter exit piping had cracked in the base metal banded area in microstructure, about 45% of the wall. Temperature was 550°F (288°C) for the first 7 years of service and the next 9 years averaged 570°F (299°C). The average temperature for the last two years was 670°F (354°C) which was about +100°F (56°C) over the plotted point. Microscopic images show decarburization and fissuring in the banded structure.

Point 53. Ammonia Plant Syngas Loop 24-inch forged pipe. Temperature 545°F (285°C), hydrogen partial pressure 2190 psi (151 bar). Ultrasonics eventually detected fissuring 46 mm (1.8 in) through the 76 mm (3.0 in) wall. Microscopic images detected fissuring/voids through 64 mm of the wall. The only attack was on the forged pipe. Hot rolled pipe in the same circuit showed no detectable attack.

The following incidents are also referenced in TR 941 but were not plotted.

Ammonia Plant Syngas converter exit line that leaked after 3000 days of service at 545°F (285°C) and 2175 psi (150 bar) hydrogen partial pressure. Material was 20CrMoV13.5. (3Cr-0.5Mo-V). The line had a history of cracking problems and high hardness. Some nitriding present and the line was post-weld heat treated below 1350°F (732°C). Showed decarburization and fissuring.

There were several submitted C-0.5Mo incidents and one source had blistering on two Ammonia Plant Shift Converters but no problems on a third.

It showed blistering, but no decarburization. Fissuring was found to be to be to 10 mm of 90 mm (0.4 in of 3.5 in) through the walls. Temperature 784 – 813°F (418 – 434°C) and hydrogen partial pressure of 165 psi (11.4 bar).

An Ammonia Plant with C-0.5Mo weldments in a line in Converter feed service showed high temperature hydrogen attack after 11 years at 563°F (295°C) and 2291-2349 psi (158-162 bar) hydrogen partial pressure. Another report was an experience the plant had with C-0.5Mo in an Ammonia Plant Desulfurizer Guard Case, with a major blistering problem at an average temperature of 662°F (350°C) and 247 psi (17 bar) hydrogen partial pressure after 115,000 hours service.

Historic (Pre-2016) Methods of NDE for HTHA Shown to be Unreliable

Since its development in the early 1970s, ultrasonic testing (UT) methods have been considered the primary non-intrusive inspection techniques for the volumetric inspection of piping and pressure vessels. This type of inspection provides an estimation of depth in addition to length and width of a defect or indication.

These early ("historic") methods proved elusive for the detection of hydrogen attack. The major challenge is that it is difficult to obtain consistent and interpretable results from one inspection period to the next, or from a different methodology/vendor at the same inspection. There were three primary historic techniques commonly evaluated for detection and characterization:

1. Ultrasonic Backscatter
2. Ultrasonic Velocity Ratio
3. Ultrasonic Attenuation

In 2012, a Joint Industry Project (JIP) was launched consisting of support from eight petrochemical companies (ranging from multi-national integrated oil companies to single site refineries). The HTHA JIP evaluated the testing results of out-of-service HTHA damaged samples and to evaluate results obtained under identical optimum "laboratory" conditions by five to seven international testing companies in the field of HTHA NDE. Twenty-five samples of plate, pipe, forgings, and fittings were gathered that had been metallurgically confirmed as having HTHA. The results of these inspections provided by the JIP group, and using historic methods, were disappointing: a "positive" confirmation rate (of less than 1 %) was recorded for the testing efforts, with most of the samples showing no damage from HTHA or any other type of anomaly. [7]

In general, these historic methods are difficult to implement practically, and the surface condition of the components can strongly influence the effectiveness and reliability of the method applied. At least half of these methods are not suited for using on the ungrounded weld caps and adjacent and heat-affected regions, and almost none of them were able to scan and record data. As a final test of the methods, samples that had been deemed free of HTHA by *all* of the vendors using historic methods were then randomly sectioned metallographically, and significant HTHA damage was noted on *all* of those samples.

At that point, it became readily apparent that there was a need for finding more reliable NDE methods for HTHA in the refining and petrochemical industries.

Modern (Post-2018) Methods of NDE for HTHA Show a Consistent, Reliable, and Accurate Pedigree

The primary purpose of NDE is detection, characterization, and sizing (surface breaking vs. subsurface, length, height, depth, crack orientation, singular flaw vs. colonies of cracking). Of secondary importance is characteristics involving productivity: screening (as measured in scan

rates of feet per minute) and surface preparation (scale or paint removal, weld protuberances, pitting) and accessibility (insulation removal, and for metal temperatures). The only methodologies available were considered practical for field use and commercially available, although proprietary methods were also allowed.

A further subset of ultrasonic methods that showed the best results on the samples used in the historic method evaluation are Time of Flight Diffraction (ToFD), Phased Array (PAUT) Ultrasonic and Full Matrix Capture/Total Field Method (FMC/FTM). Time of Flight Diffraction originated in the late 1970s as a reliable ultrasonic detection and sizing methodology. During the 1980s, several industrial trials validated ToFD as one of the most reliable ultrasonic defect detection mediums available.
Since then, ToFD has been the backbone of most AUT (Automated Ultrasonic) pipeline girth-weld inspection and has been used extensively in the power generation industry, for nuclear and fossil fuel, to detect and precisely size defects in pressure vessels, in high-pressure pipelines, and for weldments. The technique is very effective for the detection, characterization, and sizing of embedded flaws, and for accurate through-wall sizing of far-surface cracks.

The main concept of ToFD is imaging very weak ultrasonic energy, which radiates from flaw extremities. This phenomenon is known as diffraction. Low amplitude diffracted waves are best received using a simple pitch and catch probe arrangement (Figure 4).

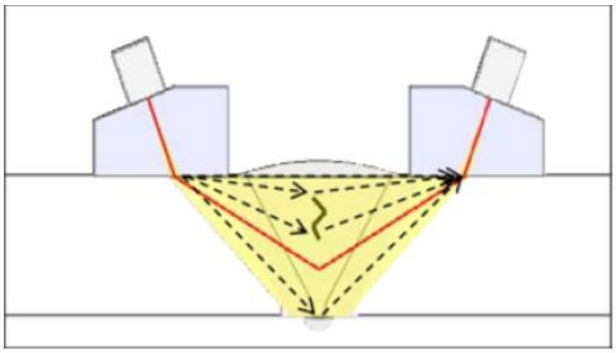

Figure 4: ToFD has the advantage of data acquisition speed to allow rapid scanning of a weld and Heat Affected Zone to identify potential sites of HTHA. [7]

The advantage of ToFD is potential data acquisition speed over any other computerized ultrasonic inspection system. The benefit of the method is rapid screening of weld and HAZ to identify potential sites of HTHA. Detection of HTHA using ToFD has been found to require careful selection of inspection parameters including transducers, filters, and contrast palettes.

Failure to optimize these can result in missing early-stage HTHA damage. Incorrect setup parameters result in poor image quality, which fails to reveal regions of connected HTHA fissures.
Due to the significance of HTHA and potential consequence of reporting such, it is vitally important that confirmatory techniques be applied. For this reason, further work has been done to understand more contemporary PAUT and FMC/TFM techniques.

The introduction and adoption of portable phased array UT units has been a leap ahead for ultrasonic inspections of critical components in various industries. Phased array UT is a mature and industrially accepted technique for volumetric inspection of components and welds for more than fifteen years.

Phased array provides an image of the inspected region and therefore allows a more intuitive interpretation of the results. The technique allows for rapid coverage of the complete examination

volume by combining sectorial scanning or electronic linear scanning with a mechanical movement, and a permanent data record for offline review and comparison with previous results.

For PAUT, observations have found that the smaller active apertures, less than 32 excited elements, are ineffective (these are the discrete areas of interrogation in the actual ultrasonic probe array). Confirmation of the presence of colonies of micro-fissures, individually ranging from 50 to 100 microns (2-4 thousandths of an inch), require significant beam focusing, achieved using large active apertures of more than 32 or even up to 64 active elements.

When using this method, caution should be taken to be mindful of reduced depth of field associated with highly focused ultrasonic beams.

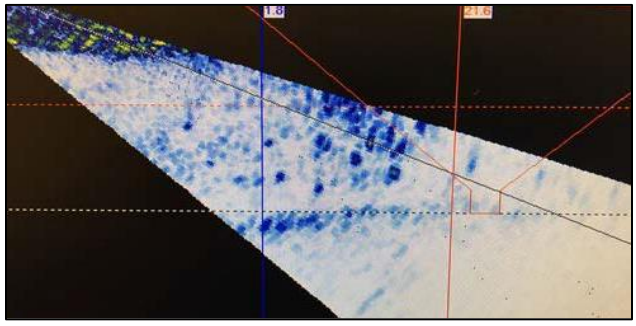

Figure 5: PAUT image reveals a colony of HTHA in the weld HAZ depicted by dark blue spots which are diffracted responses from the colony of fine HTHA fissures. [7]

The third modality for "modern" HTHA NDE in ultrasonic phased array examination involves Full Matrix Capture (FMC) and advanced focusing techniques. With the FMC technique, the elementary A-scan signals from every transmitter-receiver pair in the phased array probe are captured and recorded. In the new generation of high-end phased array units, it is now possible to process these elementary A-scan signals "live" during the inspection and generate UT images with advanced focusing techniques.

The most commonly used advanced focusing algorithm is the Total Focusing Method or TFM. The algorithm sums the elementary A-scans signals from all elements in the array to generate a frame of pixels, where each pixel is computed using a dedicated focused focal law. The TFM frames can be used for "live" interpretation, or they can be stored for each position of the probe, very similar to a "dynamic" merge view in regular phased array.

The process results in nearly ideal focusing on each point of the image, and this improved image resolution can allow for better characterization and sizing of challenging damage like HTHA.

Currently, data acquisition rates for TFM are improving rapidly. TFM effectively focuses the ultrasonic beams in sequential depth layers with potential to produce full volumetric focus throughout material cross-sectional depth.

Images produced benefit from improved axial and lateral resolution, thus providing more realistic visual rendering of HTHA damage.

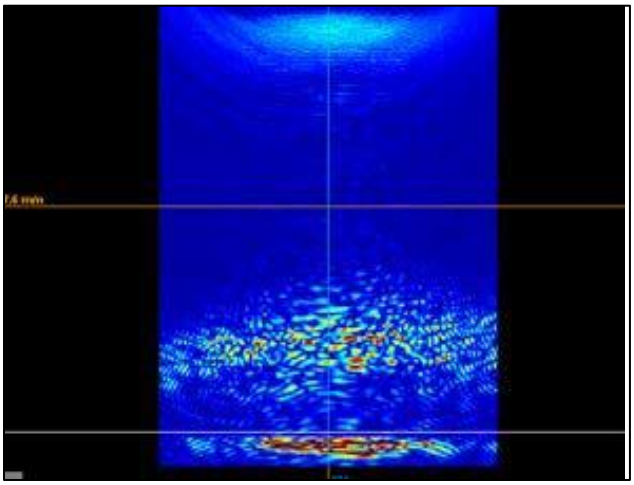

Figure 6 Example of TFM shows typical HTHA damage identified and characterized metallographically in Figure 7. [7]

All of these "modern" techniques were greatly improved by the digital signal processing and data acquisition that were being developed during the early 2000s -2010s but were not available

to HTHA NDE practitioners. However, the development and commercial deployment alone do not provide qualified NDE Service Technicians to the owner-users (producers). Therefore, in addition to this new test equipment, specialized high-level training on actual HTHA damaged specimens in a classroom environment with a proctored final written and practical exam was developed and is described below.

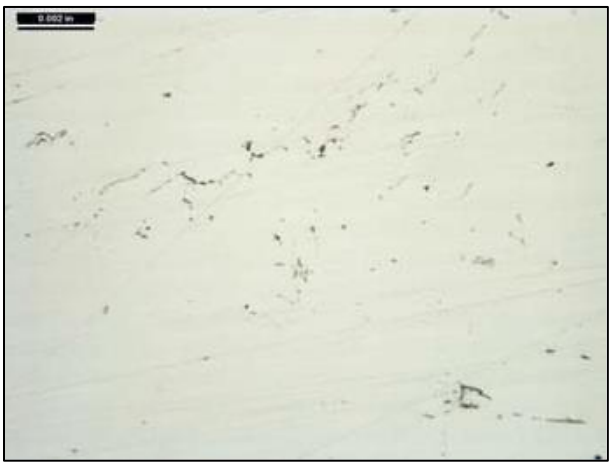

Figure 7: Ex-Service Samples that show (0.0002-micron reticle) one example of early stage HTHA damage that can be currently detected. [7]

Specialized Training in Techniques and Pattern Recognition for HTHA NDE Technicians

In the JIP NDE effort, over 100 out-of-service HTHA samples with a variety of damage morphologies have been acquired and categorized. These samples are used in specialized training for calibration and pattern recognition for the service technicians. Training and testing of NDE personnel is conducted on a test bed consisting of a variety of samples ranging from ~0.25 in (6.5 mm) pipe to 5 in (127 mm) thick plate, and includes pieces with unique geometries such as fittings, nozzles, and thickness transitions. States of damage in the samples range from early-stage incipient damage to severe through-the-wall damage.

A key component of NDE training involves both the operator collecting data on samples (personally using the probe) as well as reviewing prior-collected data (which is remotely reviewed after collection) in a proctored, uniform, and measured training environment. To date, over 150 technicians have undergone this type of training, testing and certification for HTHA NDE employing modern methods. This certification is renewed on a 3–5-year basis and ensures a level of quality and experience for the client employing these service providers. Personnel have been certified on six continents.

Evolution of API RP 586 Section 2

With the realization that the historic NDE methods previously found in the API RP 941 Annex E Table 1 were no longer the most effective methods of volumetric characterization of HTHA, a technically diverse group of industry subject matter experts began transitioning and expanding API 941 Section 6 Annex E to API RP 586 Section 2 (Inspection for HTHA). This new Recommended Practice removed the NDE component for API 941 and placed the responsible stewardship on the NDE subcommittee. [8]

This now reflects recent industry studies and includes additional details/guidance such as:

- Recommended techniques: TOFD, PAUT and FMC/TFM
- Application of multiple techniques
- HTHA specific training of NDT operators
- Emphasis on validating results with metallographic examination
- De-emphasis on AUBT (Automated Ultrasonic Backscatter Technique), ABSA (Automated Ultrasonic Signature Analysis) and some other techniques [8]

This RP was crafted and edited from 2018 and was balloted during 2021 and 2022. At the time of this paper the release of this RP is still pending. The authors do not desire to publish anything that may not have been publicly released.

API RP 586 Section Will Bridge into Fitness-For-Service Characterization

In addition to providing guidance on recommended modern NDE UT techniques as described above, API 586 looks to bridge the space from very specific and detailed NDE terminology' to useful information and data that can be directly used in by the Mechanical Integrity practitioner in an API RP 579 type of approach to assessment [9], Fitness-For-Service calculations. The API 579 work on HTHA is under concurrent development but the output of the API 586 Section 2 inspection will provide output that characterizes the damage under the following Stage 1 through Stage 4 classifications [8] shown below in Figure 8 through Figure 11:

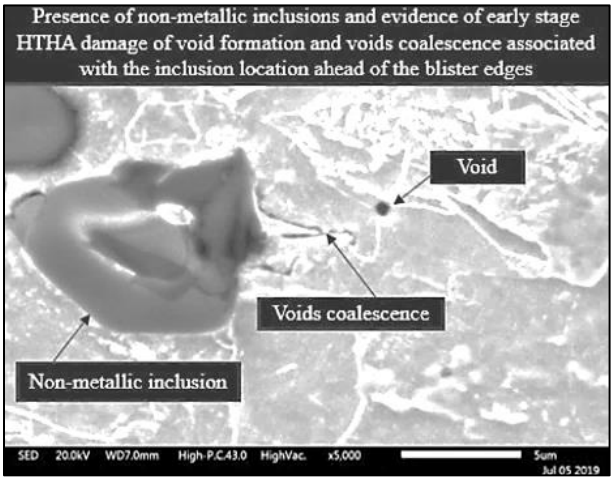

Figure 8-Stage 1. NDE indications of voids, coalescence/linking voids, and micro fissures less than 0.002" (50 microns) in individual size. [8]

Figure 9-Stage 2. An intermediate level of damage characterized as micro-fissuring or micro-blistering cluster at the sub-millimeter level around 0.002-0.004" (50-100 microns). [8]

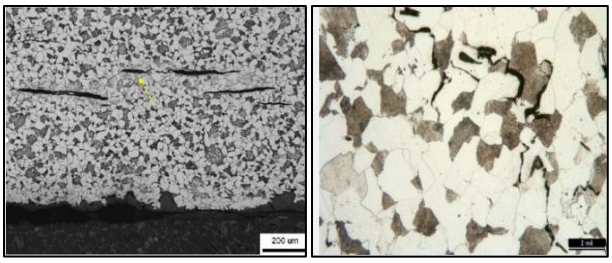

Figure 10-Stage 3. NDE indications of advanced fissures or blisters having damage in size greater than 0.004" (100 microns) up to 0.04" (1000 microns). [8]

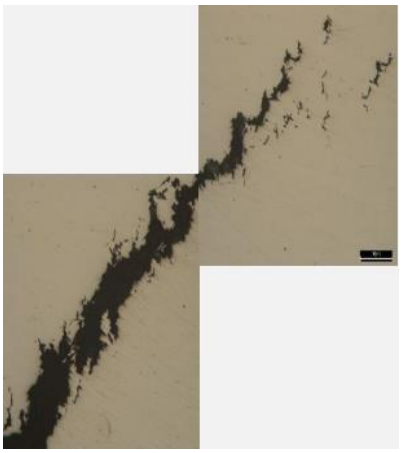

Figure 11- Stage 4. NDE indications of macro blisters or cracks, greater than 0.04" (1000 microns). [8]

API RP 941 Path

One of the overarching goals of the API Recommended Practices in Mechanical Integrity is to

provide integrity by conducting equipment evaluations throughout the anticipated life of the apparatus using past, current, and future projected operating conditions to track and project the equipment degradation over service time. The next edition of API RP 941 will no longer include Annex E on NDE but will reference API RP 586 Section 2 instead.

The API RP 941 will be revised by The API Working Group for the Time-Based Curves, which currently consists of seven Owner-Users companies, who will provide time-based design curves for Carbon Steel (PWHT and Non-PWHT) on a 30-, 50- and 100-years design basis at a given set of conditions. There are currently three models for Alternative Representation of Time-Based Curves (Temperature vs. Time) with different first principles (technical basis and methodologies) that were critically compared by a small Working Group. The goal of the current group is not to critique the existing models, but to compare the outputs of all available models on a basis of time at different temperatures as well as adding pressure regimes to the models.

There will be a focus on upper and lower bound curves to encompass short time operation above the curve (such as stripping/upsets) without additional margin (50 psi and/or 50°F, 3.4 bar and/or 28°C). The intention is to synchronize the major API HTHA efforts so that API 941 provides guidance on design only, API 579 will provide remaining life guidance as discussed below.

FFS and Life Estimation Paths

The oil refining and petrochemical industry has further used the damage mechanism (API RP 571 [12]) approach to serve as the basis for inspection planning (API 580/581 Risk Based Inspection-RBI [10,11]) and remaining life assessments (API 579-1/ASME FFS-1, Fitness-For-Service) [9]. Previously (prior to 2016), neither RBI nor FFS had any meaningful methods for HTHA assessments due to the absence of reliable, repeatable, and quantifiable NDE methods.

Recent studies on HTHA and its effect on mechanical properties have identified similarities of micro-void growth similar to classic creep. The decarburization, grain boundary voiding, and fissuring can be modeled using advanced analytic tools and various algorithms. The methane bubble nucleation, void nucleation, growth, and fissuring is more aggressive than classical creep since the methane exerts an internal pressure at or above the localized yield strength of the material.

Several engineering companies and owner-users have developed models that have addressed the kinetics of HTHA to creep-like behavior as a function of time, hydrogen cumulative exposure and stress conditions. Both experimental research and the empirical results from API 941 data have been used to refine these models over the past decade.

Now with the previously mentioned advances in NDE, the various models can be applied to better evaluate materials and equipment against HTHA. The mechanistic progress of HTHA can be assessed both in an RBI and FFS type of review to estimate prudent re-inspection intervals and also provide estimates of anticipated remaining lives so coherent run conditions or replacement schedules can be estimated.

Currently, there are a handful of HTHA models (in addition to the three that were being evaluated for the API 941 Time Based Curves) under comparison by task groups in API 941 and 579 to present guidance on the application of such technology. The anticipated desire is to limit FFS to equipment below 500 psig (34.5 barg) system pressure. Since these models are currently being actively reviewed, it is not possible to provide more detail at this time in this paper.

Summary

The key to damage mechanism assessment is the ability to reasonably detect and quantify the existing condition using some level of accurate and repeatable non-destructive evaluation methods. Such methods have been developed and implemented over the past decade.

Now that the damage can be reasonably identified, analytical models have been developed utilizing theoretical first principals, empirical data, and laboratory experience to provide the necessary validation for application of those methods.

With these tools, producers can now undertake a meaningful damage mechanism approach to review and identify susceptible piping and equipment in HTHA service, conduct targeted inspections and employ life projection methodologies for improved mechanical integrity assessments on critical process equipment in their plants.

These methods are new, evolving and require both advanced modern NDE inspections (that also require a good deal of pre-planning) and a robust review of available operation (including startup/shutdown and abnormal use conditions) to be provided for a comprehensive life projection estimation. This type of evaluation has been successfully implemented by experienced Subject Matter Experts (SMEs) in conjunction with the dedicated participation and contribution of key plant personnel.

Acknowledgments

The authors would like to acknowledge the various participants in these JIP's for their vision and ability to move this effort forward through shared resources. The API Subcommittees on Corrosion and Materials (SCCM), Inspection (SCIMI) and FFS (API RP 579) are continuing their efforts for the prudent and timely dissemination of this technology.

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