E²G INDUSTRY INSIGHTS

SPRING / SUMMER 2019 | VOLUME 7

LEVERAGING FITNESS-FOR-SERVICE AND INSPECTION TECHNIQUES TO MANAGE THE RISKS ASSOCIATED WITH HIGH-TEMPERATURE HYDROGEN ATTACK

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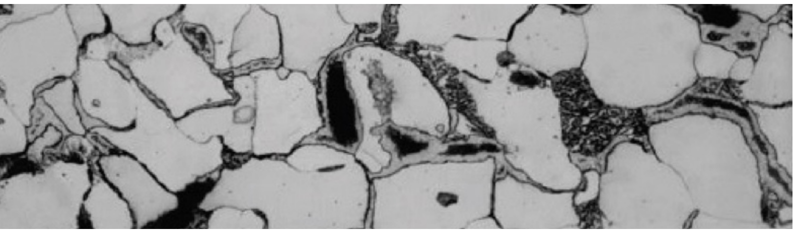


INTRODUCTION

High-temperature hydrogen attack (HTHA) is a damage mechanism that can detrimentally affect the service life of carbon steel and low-chrome pressure equipment in the petroleum refining and related industries. HTHA involves the diffusion of hydrogen into steel, where it chemically reacts with free carbon at high temperatures to produce methane. This methane then gets trapped inside small cavities and other material defects. Over time, the rising methane pressure in these cavities can cause damage at the material grain boundaries. To this end, long-term exposure to high-temperature hydrogen environments can lead to volumetric damage that can diminish the load-carrying capability of pressure equipment and accelerate the propagation of crack-like flaws. There have been several known industry failures attributed to HTHA damage as well.

This article summarizes a case study of a detailed analytical evaluation of potential HTHA damage in a vintage C-0.5Mo hydrotreater reactor. The goal of this study is to quantify the severity of HTHA damage using methods developed as part of an ongoing, multi-year Joint Industry Project (JIP) to justify continued operation of the reactor until the earliest practical replacement opportunity. HTHA damage and crack growth predictions are carried out based on documented historical operating conditions. Additionally, sensitivity in predicted remaining life to anticipated future operating temperatures is considered. Furthermore, based on state-of-the-art non-destructive examination (NDE) methods, fracture mechanics-based minimum pressurization temperature (MPT) envelopes are generated to help guide start-up and shutdown procedures that mitigate the risk for brittle fracture. Practical recommendations are also provided to facilitate the interpretation of NDE findings and to implement ongoing failure mitigation and risk management strategies, including the development of Integrity Operating Windows (IOWs), for the reactor until planned replacement.

HTHA HISTORICAL PERSPECTIVE

It has been recognized for decades that HTHA can degrade the load-carrying capacity of pressure equipment over time in the petroleum refining and related industries. Hydrogen attack was first recognized in the early 1900s when investigators reported that internal decarburization and cracking were found in plain carbon steel vessels used for ammonia synthesis [1]. In 1948, investigators of ammonia converters, heat exchangers, and piping from a DuPont process plant concluded that carbon steels containing 0.10-0.35 percent carbon were susceptible to HTHA at a hydrogen partial pressure of 350 psi (2.4 MPa) and temperatures above 570°F (300°C) [2].

In general, the resistance of steels to attack by hydrogen (and subsequently, the rate at which damage occurs) at elevated temperatures can vary significantly, depending on the material of construction and the process operating conditions (process temperatures and hydrogen partial pressure). As discussed in API 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants* [3], HTHA of steel, in general, can result in surface decarburization, internal decarburization, fissuring, methane bubble formation, delamination, or cracking of base metal and weld heat-affected zones (HAZs) and fusion lines. Furthermore, HTHA is an irreversible phenomenon resulting in degradation of mechanical strength, fracture toughness, and ductility. Pressure boundary failure may manifest itself as leaks, fires, or explosions [4].

The original set of HTHA resistance curves published by API is based on operating experience and data gathered primarily during the 1940s. These resistance curves, also known as the *Nelson Curves,* are ultimately based on data originally published by G.A. Nelson in 1949 [5]. Other early publications on HTHA include References [6-8]. The Nelson Curves graphically represent *safe* operating zones for common pressure vessel and piping materials of construction, as related to operating temperatures and hydrogen partial pressures. The regions of acceptable or *safe* operation are considered to be below the Nelson Curves. Furthermore, most equipment owner-users typically assign a safety margin (as recommended in API 941 [3]) to achieve operating conditions that are a specified distance below the curve for a given material. The current version of the Nelson Curves from the Eighth Edition of API 941 [3] are shown in Figure 1.

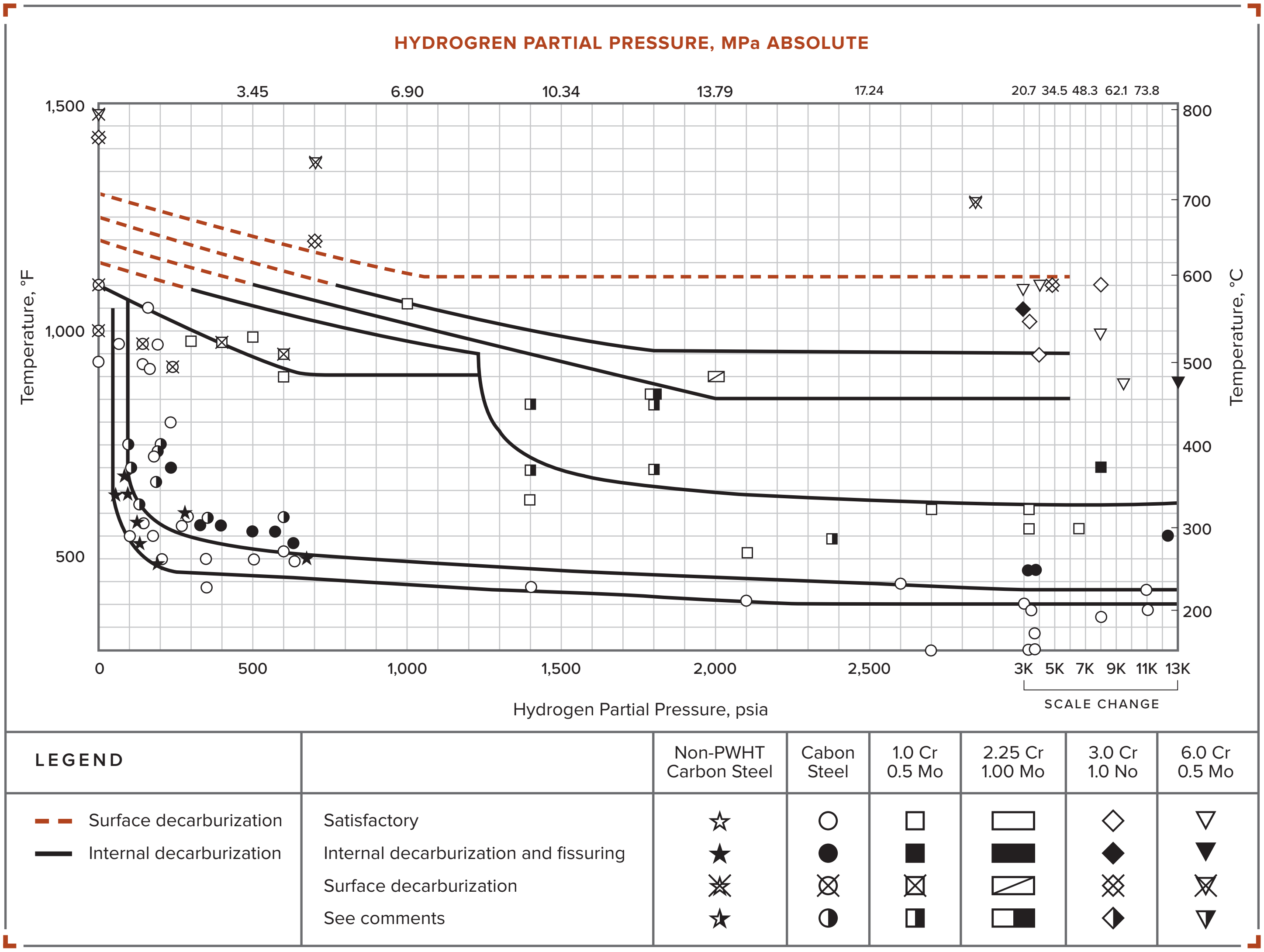


Figure 1. Operating Limits for Steels in Hydrogen Service to Avoid HTHA [3]

Supporting data for the Nelson Curves is overlaid in Figure 1. These data points include successful operation, decarburization (internal and surface) cracking and fissuring, and failures. The dotted lines at the top of Figure 1 reflect the propensity for surface decarburization of steels while they are in contact with hydrogen. The solid lines represent the propensity for steels to decarburize internally with resultant fissuring and cracking. Furthermore, these points were obtained from a variety of commercial processes and laboratory experiments. The combination of elevated temperature and low hydrogen partial pressure generally favors surface decarburization, without internal decarburization and fissuring. In contrast, the combination of low temperature, but above 400°F (204°C), and high hydrogen partial pressure, above 2200 psia (15.17 MPa), typically favors internal decarburization and fissuring, which can eventually lead to the initiation and propagation of crack-like flaws. At elevated temperatures and high hydrogen partial pressures, both damage mechanisms may be active [3].

The data to support the Nelson Curves was obtained from a variety of documented failures and successful operating scenarios at high-temperature and high hydrogen partial pressure [5] (some data was obtained from unpublished reports and private communications). While temperature and hydrogen partial pressure data were not always known precisely and the curves themselves are not inherently time-dependent, the accuracy is often considered to be sufficient for commercial use. In Figure 1, satisfactory performance is plotted only for samples or equipment exposed to operation for at least one year. Unsatisfactory performance from laboratory or plant data is plotted regardless of the length of exposure time. Based on these compiled data points, it is evident that higher-chrome materials generally have better resistance to HTHA relative to carbon and low-alloy steels. To this end, the addition of carbide stabilizers to steel reduces the tendency toward internal fissuring. Elements such as chromium, molybdenum, tungsten, vanadium, titanium, and niobium form more stable alloy carbides that resist breakdown by hydrogen and thereby decrease the propensity of methane formation that can lead to HTHA [6].

RECENT INDUSTRY INITIATIVES

An ongoing JIP [9-11] led by E²G, now in its sixth year, has resulted in the development of improved NDE techniques for detecting HTHA and advancements in predicting HTHA damage as a function of time and operating conditions. Additionally, Reference [12] summarizes aspects of the developments from the E²G JIP, including advanced inspection and HTHA analysis techniques. Furthermore, References [13,14] offer examples of how fitness-for-service techniques (anchored in the methods provided in API 579-1/ASME FFS-1, *Fitness-For-Service* (API 579) [15]) such as detailed stress analysis and fracture mechanics can be leveraged to manage the risks associated with operating potentially damaged equipment in environments prone to HTHA damage. A notable recent publication that investigates some of the historic data sources and correspondence that form the basis of the current Nelson Curves and includes relevant information regarding the removal of the historic C-0.5Mo curve is Reference [16]. This publication also highlights some of the unknown and missing data incorporated into the existing Nelson Curves. Two recent publications by the Health and Safety Executive (HSE) in the United Kingdom that focus on managing equipment prone to HTHA damage are References [17,18]. Additionally, Reference [19] is another recent publication on HTHA by The Engineering Equipment and Materials Users Association (EEMUA) out of the United Kingdom, focused on managing in-service equipment in high-temperature hydrogen environments.

C-0.5Mo HTHA SUSCEPTIBILITY

Over the years, issues have been encountered with the original, empirical limits set for C-0.5Mo steels [4]. Subsequently, most equipment owner-users no longer specify C-0.5Mo steel for new or replacement pressure components used for operation above the post-weld heat treated (PWHT) carbon steel Nelson Curve (see Figure 1) because of the uncertainties regarding its performance after prolonged high-temperature and high-pressure hydrogen exposure. Since 1970, a series of unfavorable service experiences with C-0.5Mo steels has reduced confidence in the position of the original C-0.5Mo curve [20]. In the Second Edition (1977) of API 941 [21], the C-0.5Mo curve was lowered approximately 60°F (33°C) to reflect a number of plant experiences that involved HTHA of C-0.5Mo equipment. In the Fourth Edition (1990) of API 941 [22], the C-0.5Mo Nelson Curve was removed altogether due to additional cases of HTHA of C-0.5Mo steel equipment occurring by as much as 200°F (111°C) below the curve. At that time, experience had identified 27 instances of HTHA below the 1977 curve [3]. Figure 2 shows magnified images of HTHA damage in service-exposed C-0.5Mo material (from Reference [4]).

In general, C-0.5Mo steels vary significantly in their resistance to HTHA. In fact, some heats seem to have HTHA resistance only marginally better than carbon steel. Furthermore, the current edition of API 941 [3] indicates existing C-0.5Mo steel equipment that is operated above the PWHT carbon steel curve

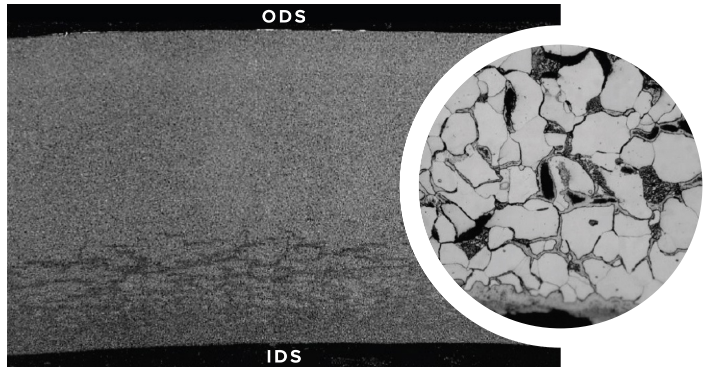


Figure 2. *Photomacrograph at 3.5x (left) and Photomicrographic at 400x (right) showing Decarburization and Hydrogen Damage in C-0.5Mo Near the ID Surface of Service-Exposed Sample [4]*

in Figure 1 should be inspected to detect HTHA. Important variables to consider when prioritizing C-0.5Mo equipment for inspection include severity of operating conditions (hydrogen partial pressure and temperature), thermal history of the steel during fabrication, stress, cold work, cladding composition, and thickness (if present). Accurate documentation of historical operating conditions is crucial when evaluating relative HTHA risk for different components. Furthermore, a lack of documented pressure and temperature trends introduces additional unknowns and uncertainty into any HTHA analysis, and oftentimes, conservative assumptions must be employed in lieu of actual measured process data.

Welding Research Council (WRC) Bulletin 548 [4] provides information on the mechanical properties of different C-0.5Mo samples exposed to different heat treatments and after high-temperature hydrogen service exposure. An example of impact energy for a service-exposed C-0.5Mo sample as a function of temperature is shown in Figure 3. This figure shows that upper shelf fracture toughness is likely not achieved until a temperature of 200°F or higher is reached.

Figure 4 shows the influence of methane and hydrogen concentrations on Charpy impact energy, with higher concentrations of both decreasing fracture toughness. This figure shows the detrimental effect of methane concentration on the mechanical properties as a function of specimen distance from the inside surface. Additionally, yield and ultimate tensile strength both increase as the concentration of methane (and hydrogen) decreases, and the ductility increases as the concentration of methane (and hydrogen) decreases. In this same study, Lundin et al. [4] concluded that in the service-exposed condition, precipitation hardening of the ferrite may have occurred, which may be responsible for the reduced impact energy (which can be correlated to fracture toughness) compared to more rapidly cooled heat-treated materials. Additionally, this study concluded that higher levels of bainite in the microstructure of C-0.5Mo generally promoted higher levels of toughness. Furthermore, quenched and tempered or normalized and tempered are considered to be the optimum heat treatments to achieve superior toughness and strength in C-0.5Mo steels.

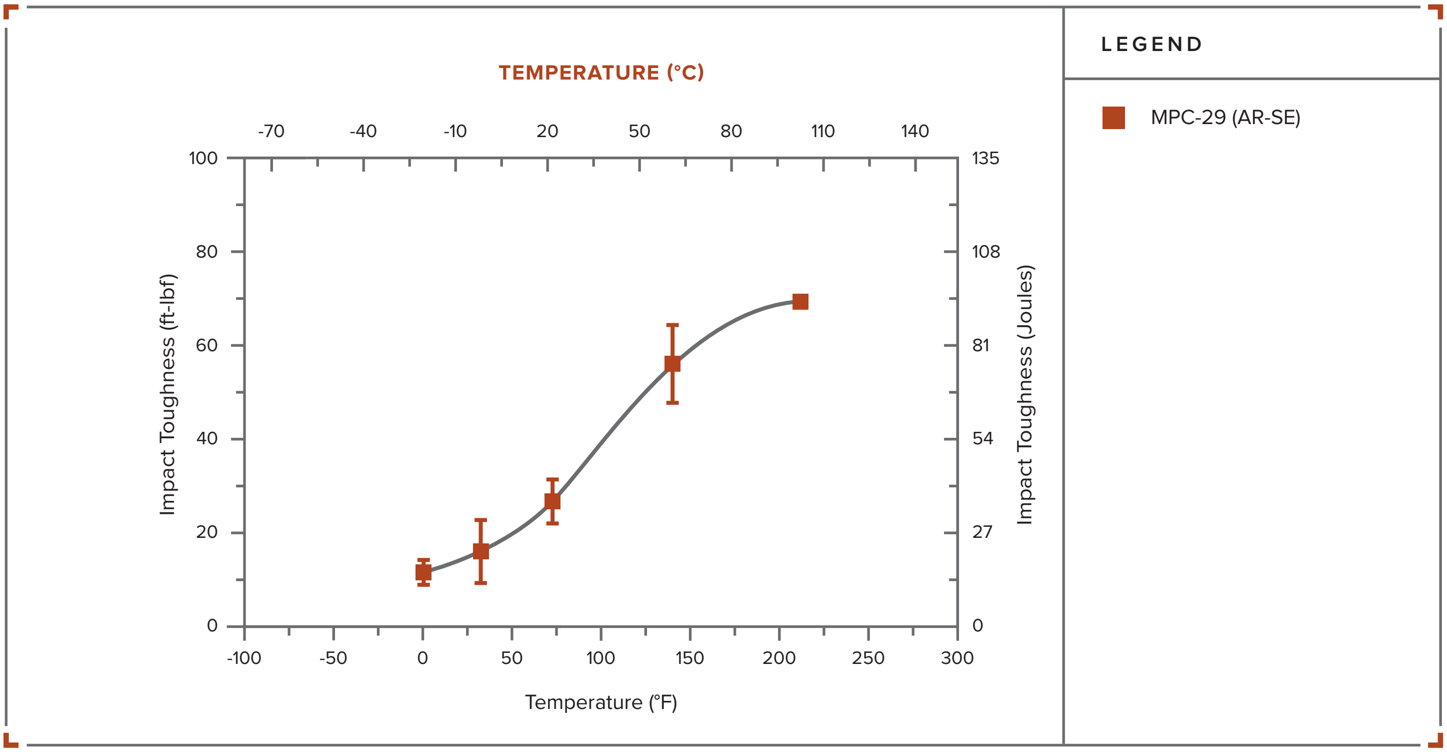


Figure 3. *Impact Energy vs. Temperature for Service-Exposed C-0.5Mo [4]*

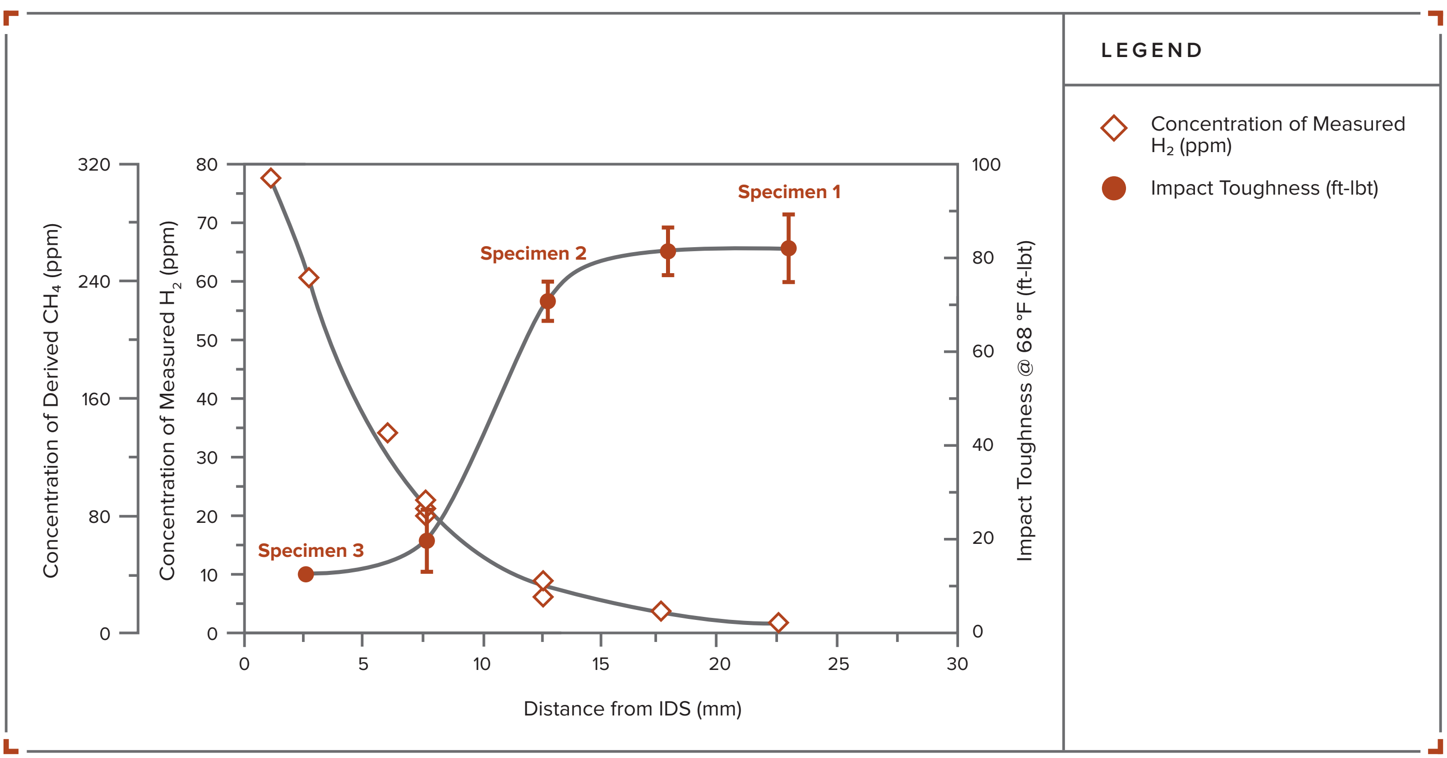


Figure 4. *Methane Concentration vs. Impact Energy for C-0.5Mo [4]*

HTHA DAMAGE MECHANICS

As discussed extensively in References [9-11], the mechanism of HTHA is characterized by volumetric material damage and possibly, the propagation of crack-like flaws (typically at or near welds). Figure 5 shows a schematic of how material can become weakened over time due to the mechanism of HTHA. In summary, damage starts through the diffusion of hydrogen into steel, where it chemically reacts with free carbon at high temperatures to produce methane. This methane then gets trapped inside small cavities and other material defects. Over time, the rising methane pressure in these cavities can cause damage at the material grain boundaries. Furthermore, long-term exposure to high-temperature hydrogen environments can lead to volumetric damage that can diminish the load-carrying capability of pressure equipment and accelerate the propagation of crack-like flaws. Additionally, micro-cracks tend to form at grain boundaries and can coalesce to form macro-cracks.

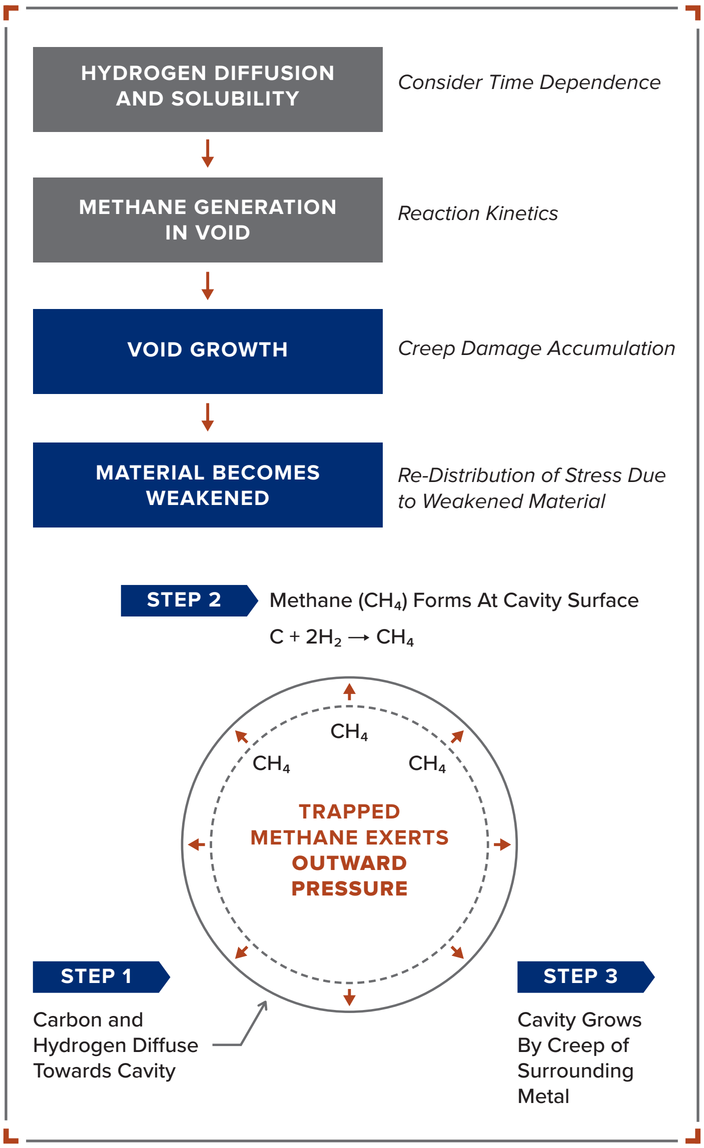


Figure 5. *Schematic Showing the Mechanism of HTHA Damage [13]*

Figure 6 shows an example of a HTHA-driven crack-like flaw near a weld HAZ as well as an example of both volumetric HTHA damage and cracking occurring near a different weld (where volumetric damage and blistering can be seen ahead of the inside surface-initiated crack tip). While many documented HTHA failures are attributed to cracking near welds, this figure highlights that these two mechanisms are linked in that volumetric damage and the coalescence of methane-filled micro-voids can degrade material strength and toughness and accelerate crack propagation. Because of this, crack growth predictions summarized herein account for volumetric HTHA damage (where damage is calculated as a function of time and operating conditions). Furthermore, crack growth is then accelerated by calculated volumetric damage [9-11].

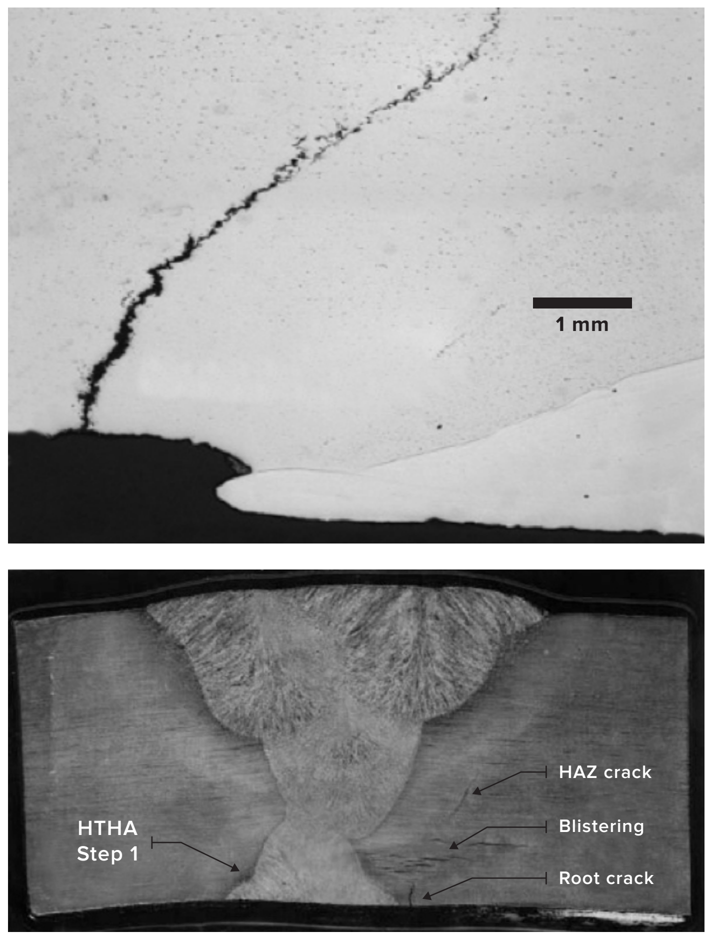


Figure 6. *Example of a HTHA-Driven Crack-Like Flaw (top) and HTHA Coupled Volumetric and Crack-Like Flaw Damage (bottom) [9]*

While the details of the HTHA damage model employed in this study that has been developed through the ongoing JIP [9-11] are not covered in this article for the sake of brevity, the model fundamentally treats volumetric HTHA damage as time-dependent, methane-enhanced creep (based on Part 10 of API 579 [15]) using MPC Omega creep model, but with an additional driving force (stress) due to methane pressure. As discussed above, the calculated volumetric damage is used to evaluate protection against structural collapse and to accelerate crack growth predictions.

NON-DESTRUCTIVE EXAMINATION (NDE) TECHNIQUES

As discussed in Reference [23], NDE has historically been used to ensure the quality of new fabrication in addition to assessing the integrity of service-aged equipment. Although there have been published recommended inspection techniques for HTHA in the past, many owner-users have found notably varying results on the same piece of equipment (raising questions about confidence in the methods to consistently and accurately identify HTHA damage in pressure equipment). Based on an ongoing JIP [9-11], data analysis should consist of many forms of raw ultrasonic data, including time-of-flight-diffraction (TOFD), phased array ultrasonic testing (PAUT), and UT backscatter data.

The advantage of TOFD is the data acquisition speed over other computerized ultrasonic inspection systems, the benefit of which principally allows rapid screening of welds and HAZs to identify potential areas of HTHA. Detection of HTHA using TOFD requires careful consideration pertaining to inspection parameters, including transducers, filters, and contrast palette. Failure to optimize these parameters can result in missing early stage HTHA damage [23]. To highlight this point, Figure 7 shows two TOFD scans of a weld with HTHA damage. One scan has incorrect set-up parameters (thus showing no apparent damage) and the other has the correct parameters (clearly showing HTHA damage). If HTHA damage is identified using TOFD, follow-up targeted PAUT is often warranted to further characterize the severity and extent of the damage. Again, proper tuning of parameters is imperative.

Ultimately, the focus of this article is not on HTHA inspection techniques. Nevertheless, the accuracy of recently developed and specialized NDE methods has improved in recent years to the point that a properly trained inspector can reliably detect significant HTHA damage. To this end, it is essential that inspectors be properly trained on an extensive catalog of service-aged samples, ranging from incipient damage to advanced HTHA damage in a variety of test forms, shapes, and thicknesses that represent what will ultimately be inspected in the field. Furthermore, the training should be in-depth with a focus on understanding HTHA damage manifestation, advanced UT applications, the fine-tuning of test equipment parameters, and data acquisition from a variety of thicknesses and states of material degradation. Sources of false positives should also be discussed (material inclusions, stepwise HIC damage, and the effects of weld cladding issues). This training should incorporate hands-on testing as well as discussion of the theoretical approach and off-line data analysis methodologies [23]. In this article, the summarized hydrotreater reactor case study involved the use of the above mentioned NDE techniques by a fully trained (and certified) inspector. These inspection findings are coupled with the analysis methods outlined herein to understand the risk of continued (short-term) reactor operation.

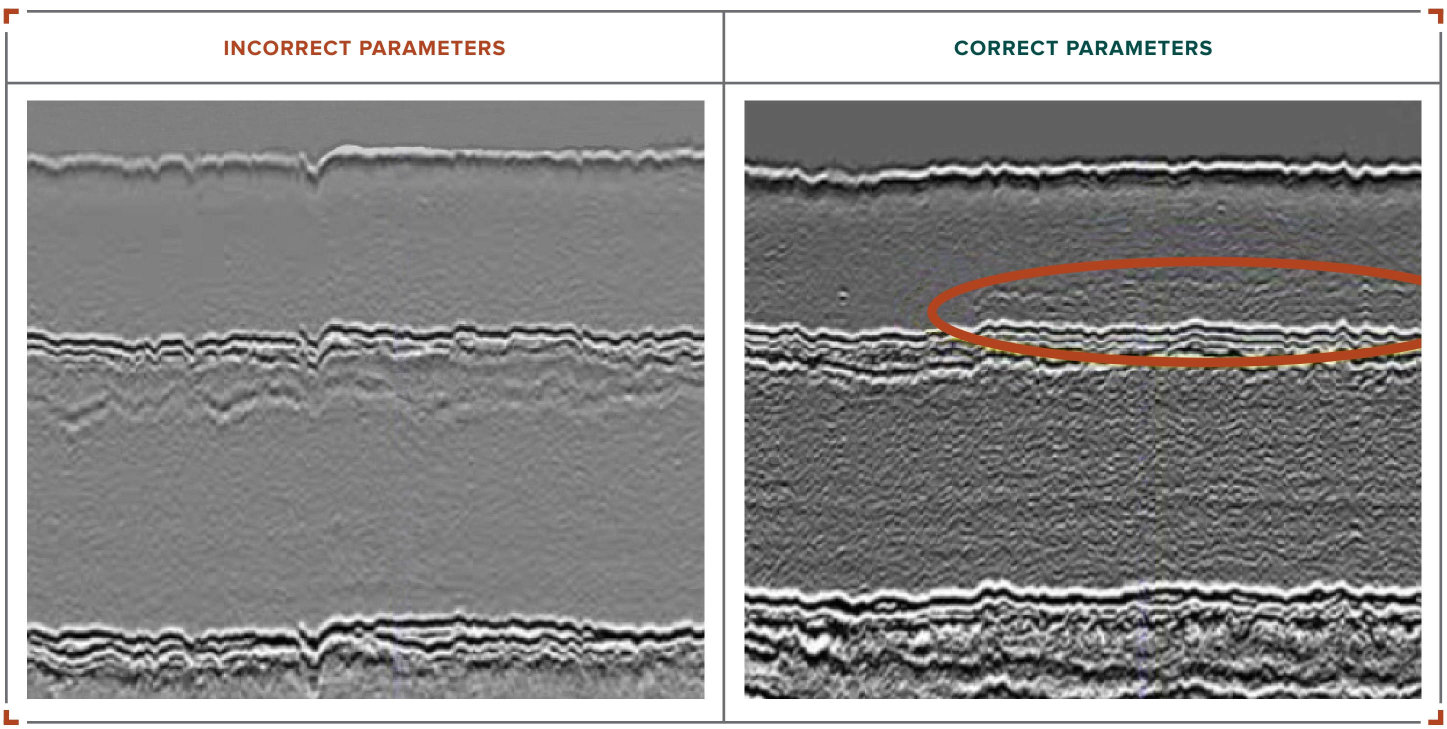
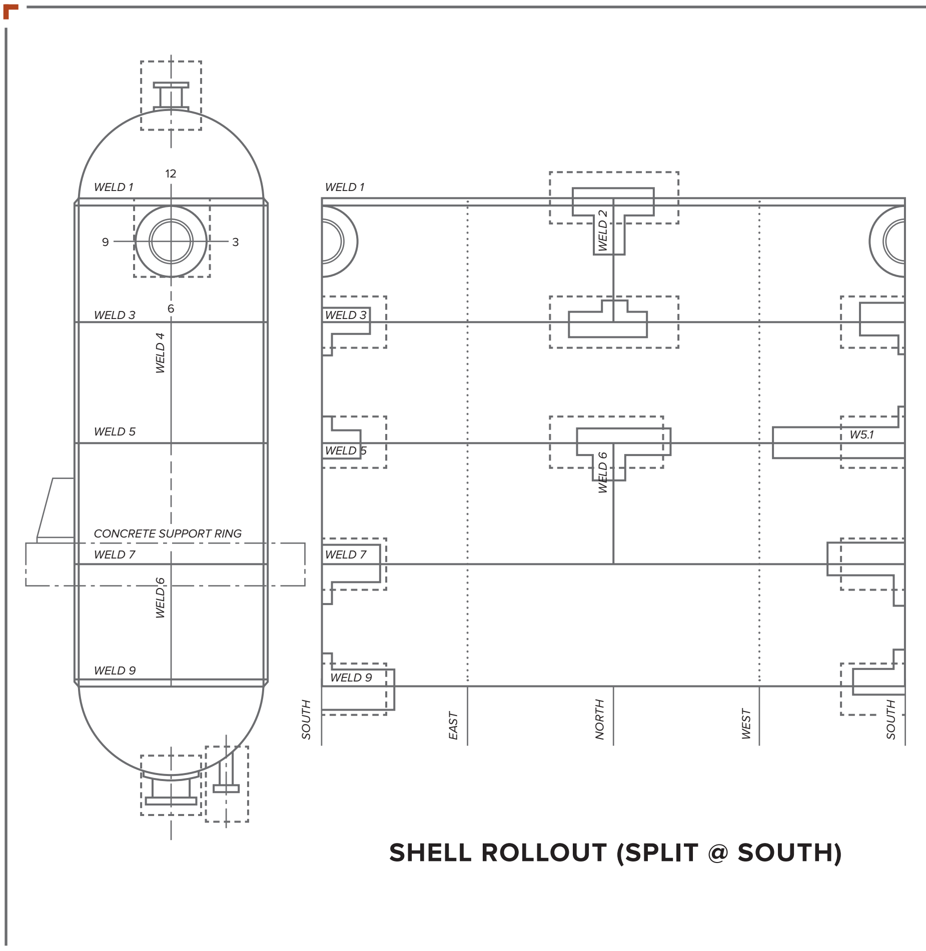


Figure 7. *Weld with No Apparent HTHA Due to Incorrect TOFD Set-Up Parameters (left) and TOFD Scan of the Same Weld with the Correctly Tuned Parameters, Showing HTHA Damage (right) [23]*

HYDROTREATER REACTOR CASE STUDY

This article provides a summary of a case study on an in-service hydrotreater reactor that received targeted inspection for HTHA damage. The reactor inspection map (including a roll-out of the cylindrical shell) is provided in Figure 8 to show the targeted weld locations that were examined. Longitudinal-to-circumferential weld T-junctions were targeted in addition to nozzle and manway-to-shell junctions. In summary, the inspection identified possible incipient HTHA damage and a few damaged regions near welds consistent with crack-like flaws (potentially originating as fabrication defects).

After the inspection, HTHA damage calculations were carried out and MPT envelopes were generated to evaluate the likelihood of failure and to provide perspective on safe pressurization procedures to avoid brittle fracture, respectively. A summary of the hydrotreater reactor design details is offered in the list below:



Year of Construction	1975
Design Code	ASME Section VIII Division 1 (1974) [24]
Base Metal	SA-204 Grade B (C-0.5Mo)
Design Pressure	629 psig
Design Temperature	775°F
Inside Diameter	7 feet, 3 inches
Cylinder Wall Thickness	1.750 inches total
Cladding	347 stainless steel, 0.100-inch min. thickness
Radiography	100% (joint efficiency = 1.0)
PWHT:	Yes, specified at 1175°F-1200°F

Figure 8. *Reactor Inspection Map with Roll-Out of Cylindrical Shell*

In this case, approximately 10 years of operating hydrogen partial pressure and temperature data were compiled, and histograms generated as follows:

- A median filter was applied to daily average data to remove noise.
- The noise was isolated and its standard deviation was found. Approximately 2 standard deviations of H_2 partial pressure (25psia) and approximately 1 standard deviation of temperature (10°F) were added to the clean data. The resulting histograms sit above approximately 99% of the original data.
- The temperature and pressure peaks indicated were added to bound the remaining 1% of data points.
- Downtime filters were then added.
- The cleaned data was entered into an algorithm to generate a histogram.

Based on this approach, the resulting pressure and temperature histograms are plotted in Figure 9 (note there is a primary and secondary axis). This 10-year window of available operating conditions is then extrapolated and assumed to be applicable for the entire lifetime of the reactor to-date (since 1975). To offer additional perspective on typical historical operating conditions, operating data points are overlaid onto the current as-welded and PWHT carbon steel Nelson Curves (with the latter being the current recommended limit for C-0.5Mo) in Figure 10. This figure demonstrates that historical operating trends for the reactor in question generally fall above the PWHT carbon steel curve, highlighting the potential for HTHA damage.

Using the established hydrogen partial pressure and temperature histograms shown in Figure 9, HTHA damage calculations are carried out based on the E²G JIP [9-11]. Additionally, two different future operating temperatures are considered: 625°F and 650°F. For both assumed temperatures, crack growth calculations are performed based on different flaw sizes. These crack growth calculations are based on data published by Shewmon and Xue [25] with factors of safety applied. It is recognized that this crack growth data is based on carbon steel base metal. Nevertheless, this baseline data is leveraged until ongoing crack testing results that include welds and C-0.5Mo samples (as part of the ongoing JIP [9-11]) become available. The concept of these crack growth estimates is to determine if a current crack-like flaw is likely to propagate to critical dimensions (determined using the fracture mechanics approach described below) before planned reactor replacement. To this end, reactor replacement is the recommended long-term strategy given the vintage of the reactor and the identified potential HTHA damage. Nevertheless, in the short-term, risk mitigation strategies including establishing technically based pressurization approaches to avoid brittle fracture during start-up or shutdown and understanding the risk of crack growth due to HTHA are employed.

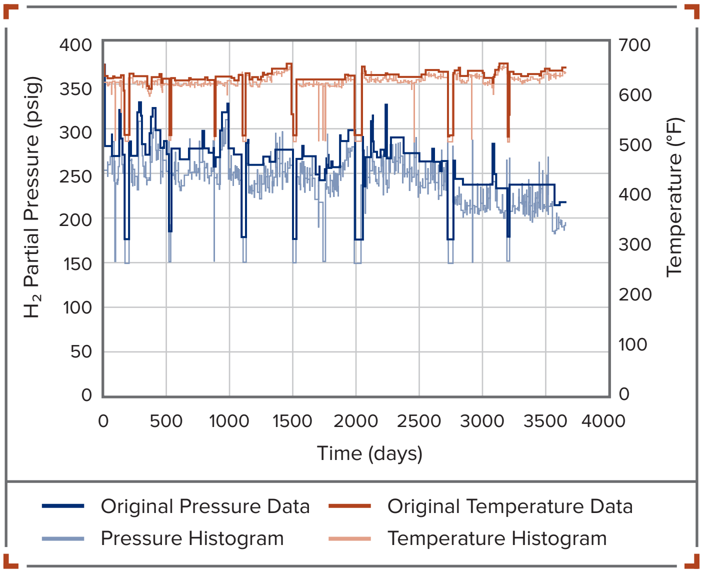


Figure 9. *Histograms of Hydrogen Partial Pressure and Temperature Data*

MINIMUM PRESSURIZATION TEMPERATURE (MPT) APPROACH

The fracture mechanics-based approach for evaluating the risk for brittle fracture in the hydrotreater reactor discussed in this article is anchored in the Failure Assessment Diagram (FAD). The FAD approach was adopted in API 579 [15] because it provides a convenient, technically based method to determine the acceptability of a component with a crack-like flaw.

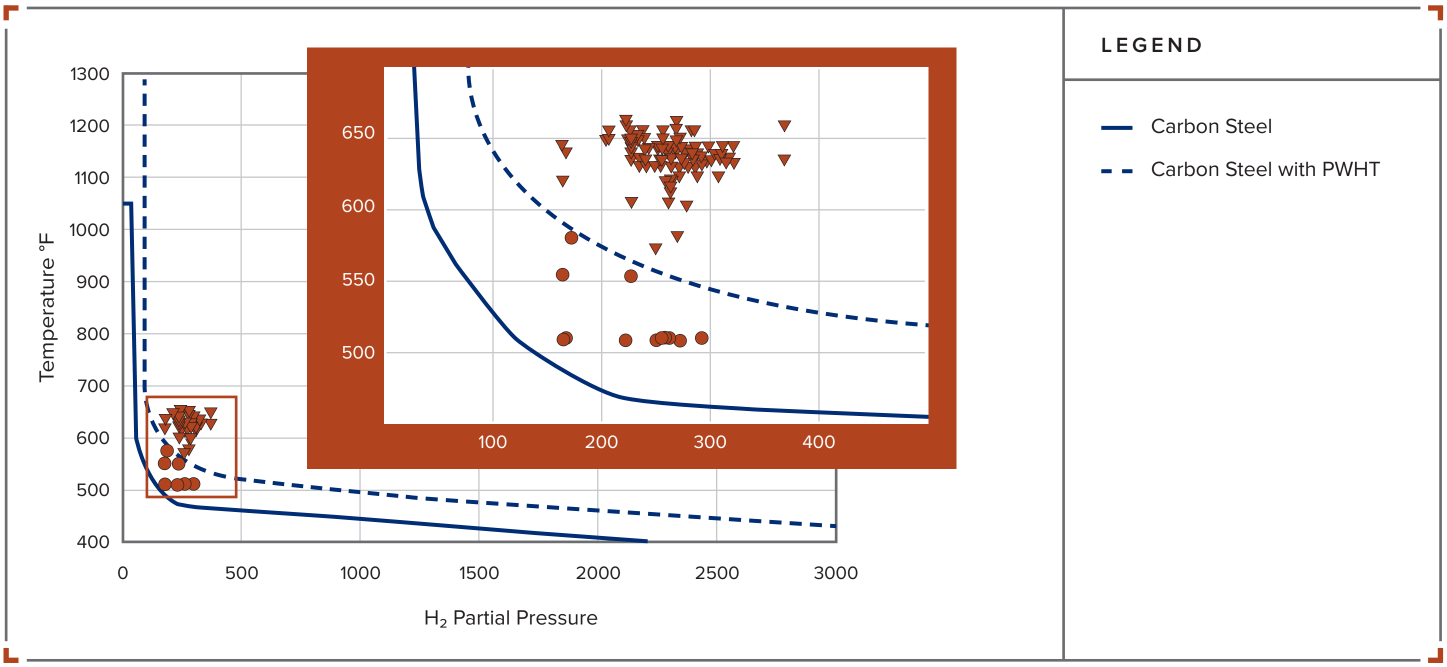


Figure 10. *Operating Hydrogen Partial Pressure and Temperature Data Overlaid on Nelson Curves*

In this method, the driving force for failure is measured by two distinct criteria: unstable fracture and limit load. Linear elastic fracture usually controls failure in cracked components fabricated from a brittle material, and plastic collapse at a limit load typically controls failure if the component is fabricated from a material with high toughness (high ductility). Elastic-plastic fracture occurs between these two extremes. In the analysis of crack-like flaws, the results from a stress analysis, stress intensity factor, limit load solutions, material strength, and fracture toughness are combined to calculate a toughness ratio and a load ratio for primary stress. These two quantities represent the coordinates of a point that is plotted on a two-dimensional FAD to determine acceptability. If the assessment point is on or below the FAD curve, the component is suitable for continued operation. As outlined in References [26, 27], an iterative approach (varying pressure and temperature) can be employed to generate an MPT envelope (safe operating pressure-temperature region) for a given reference flaw size using the FAD. The fracture toughness employed in this study is based on the use of the Fracture Toughness Master Curve (Master Curve) [28] in conjunction with the FAD methodology described in API 579 [15]. In this case, the impact energy and fracture toughness data in WRC Bulletin 548 [4] for service-exposed C-0.5Mo is used to shift the Master Curve to match available test data.

HTHA & MPT ANALYSIS RESULTS

The flow chart shown in Figure 11 summarizes, from a high level, the overall approach for attempting to qualify the fitness-for-service of the hydrotreater reactor with potential HTHA damage. This figure demonstrates the interaction between inspection findings and performing advanced analysis (such as MPT and crack growth calculations) to qualify the identified damage. Additionally, the overall process for maintaining safe operation is outlined. Violating the recommended MPT envelopes (possible upset scenario) or shutting down results in the recommendation for follow-up inspection to quantify damage progression.

Following completion of the inspection summarized above, the most limiting defects were evaluated (actual measured flaw dimensions) using the MPT assessment approach described above, and buffers or margins of 25°F and 50°F were applied to the most limiting MPT envelope. Figure 12 shows a plot of these two MPT curves. Any pressure-temperature combination below or to the right of a given MPT curve is considered to be acceptable to avoid brittle fracture. Additionally, this figure shows actual operating pressure-temperature points representative of typical start-ups and shutdowns. Since typically the coldest metal temperatures occur during start-up or

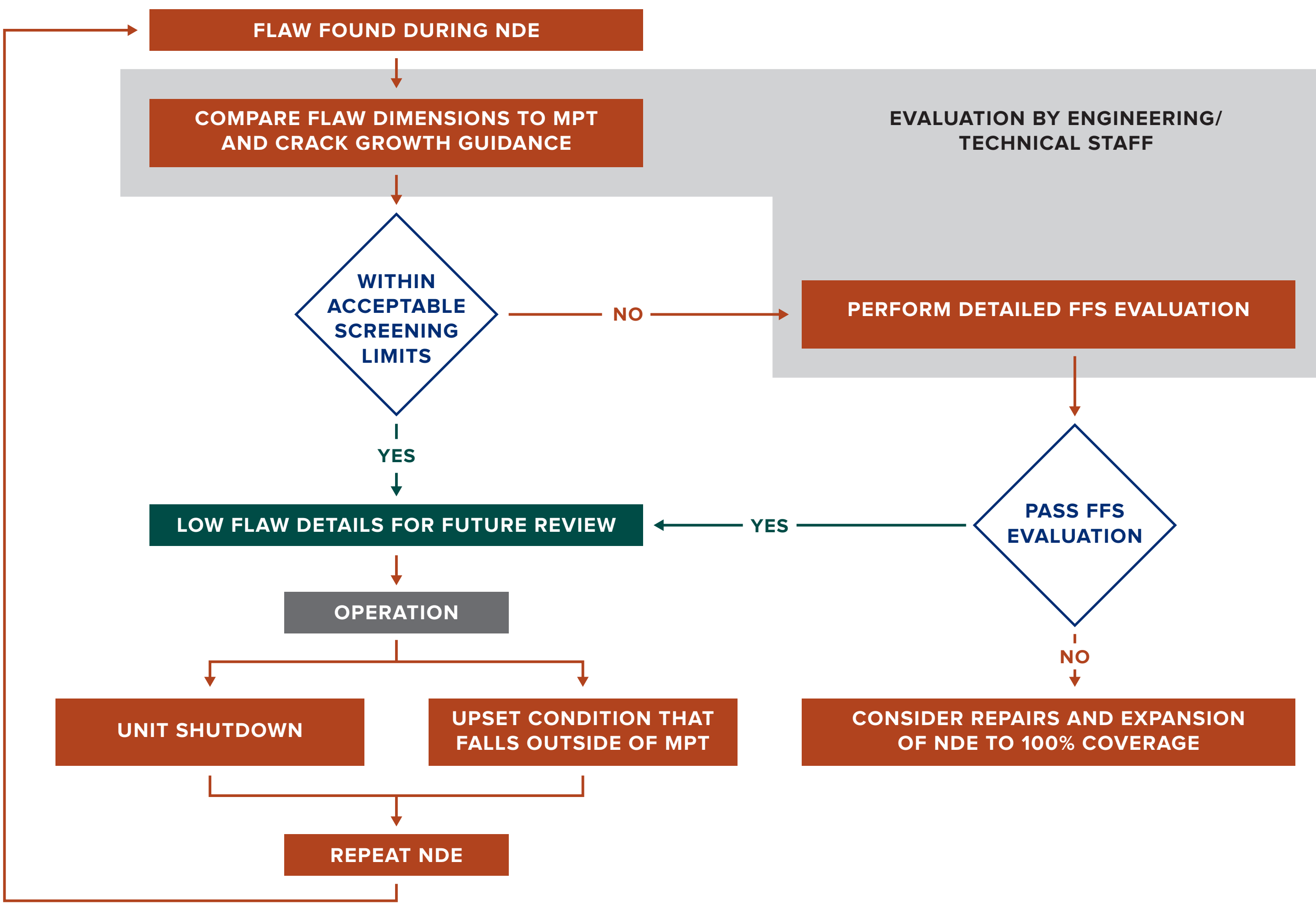


Figure 11. Flow Chart of Fitness-For-Service Analysis Approach

shutdown, the risk for brittle fracture is generally the highest at these times. The reason for invoking some margin or buffer on the most limiting MPT curve is to attempt to account for analysis unknowns such as fracture toughness and the possible presence of a larger defect that was not identified during the targeted inspection (that is, because 100 percent coverage of all pressure boundary welds was not carried out). Figure 12 highlights that historical pressurization procedures technically violate these proposed MPT envelopes. The MPT curve with a 50°F buffer indicates that essentially no pressurization is recommended for temperatures below 150°F. While this may seem overly limiting, the extent of the identified damage, coupled with potentially conservative fracture toughness assumptions and the crack driving forces associated with weld and cladding residual stress, result in limiting pressurization curves, even at little-to-no internal pressure.

Given limiting pressurization recommendations and the identification of damage indicative of HTHA, the long-term strategy for the hydrotreater reactor in question is replacement; however, there is an approximately two-year operating window before this replacement is feasible. To manage the overall risk in the short-term, modified pressurization procedures are necessary. As a practical means to achieve reactor metal temperatures of approximately 200°F before pressurization, external steam tracing was applied to the reactor pressure boundary. Once this metal temperature is achieved, the intent is to keep operating (pressure-temperature) points within the proposed MPT curve with a 50°F buffer.

Since HTHA is a time-dependent mechanism and because defects characterized as crack-like flaws were identified in some of the reactor pressure boundary welds, crack-growth estimates are carried out for different flaw depths with different aspect ratios (length-to-depth ratios). Figure 13 shows operating time (in years) for a given crack-like flaw *(t/4, t/3,* and *t/2)*, in the cylindrical shell remote from structural discontinuities, to reach critical dimensions or reach 80% through-wall based on the crack growth correlations in Reference [25]. This figure includes a safety factor of two on all points since the baseline crack growth data from Reference [25] is for base metal only and not welds (where residual stresses, material property mismatches, and geometric effects could accelerate crack growth). Furthermore, along the horizontal axis of Figure 13, sensitivities to different flaw length-to-depth aspect ratios are evaluated (from 6:1 up to 24:1). As expected, longer crack-like flaws have a shorter predicted remaining life. Additionally, this figure shows predictions for future operating temperatures of 625°F (blue curves) and 650°F (orange curves). Again, as expected, the higher future operating temperature results in more rapid crack growth rates. It is noted that inspection intervals of half the predicted remaining life (or less) are generally recommended as well.

Higher stress states (for example, near structural discontinuities) result in more limiting remaining life predictions for a given crack-like flaw [29]. As discussed herein, crack growth predictions are a function of calculated volumetric HTHA damage as well. Based on these crack-growth predictions (with likely conservative safety factors included), confidence is gained that in the short-term, it is unlikely that a current crack-like flaw in the reactor will grow to a critical size due to HTHA. This determination coupled with the recommended pressurization procedure outlined above reflects a means to manage the risk associated with operating this hydrotreater reactor (with known potential

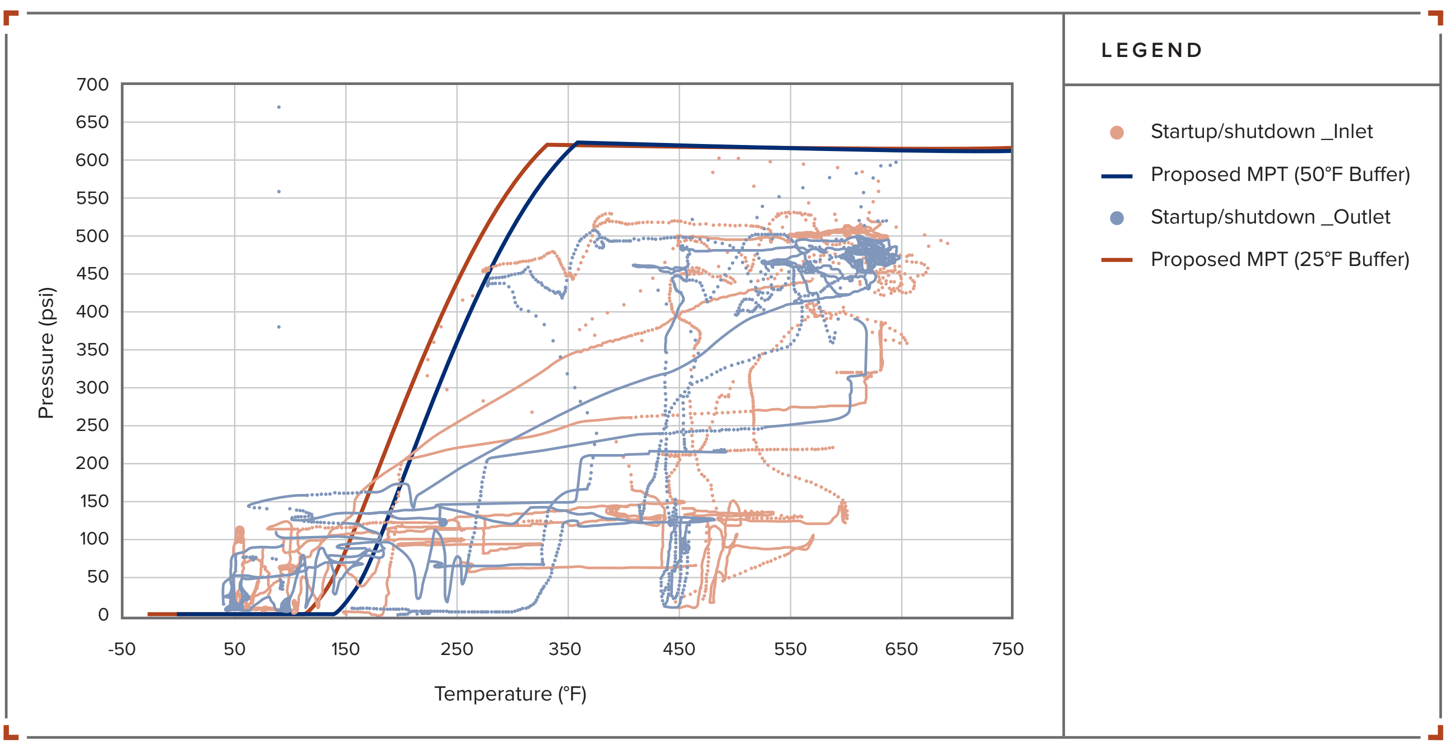


Figure 12. *Proposed MPT Envelopes with 25°F and 50°F Buffers Relative to the Most Limiting Crack-Like-Flaw*

HTHA damage) in the short-term, until planned replacement can be carried out. Additional MPT and crack growth considerations for this case study are provided in Reference [29].

INTEGRITY OPERATING WINDOWS (IOWs)

For the reactor evaluated in this article, IOWs already existed to mitigate long-term damage. However, following completion of the HTHA inspection effort, HTHA crack growth predictions, and MPT calculations summarized herein, new, more stringent IOWs were implemented to achieve safe pressurization procedures to avoid brittle fracture, and maximum metal temperature limits were specified to reduce the risk for time-dependent HTHA crack growth. These new IOWs were implemented through an existing Management of Change (MOC) process that goes beyond typical administrative controls and ensures that proper personnel are immediately notified if any established IOWs are violated. Additionally, this MOC process includes periodic reviews of specified IOW limits, measured reactor process data (operating pressures and temperatures, etc.), and overall unit operating trends. Some unit process changes were also required to carry out recommended pressurization procedures and to stay within maximum metal temperature limits.

In this case, external steam tracing was installed on the reactor to achieve a bulk pressure boundary metal temperature of 200°F prior to reactor pressurization to avoid brittle fracture, and the proposed MPT envelope with a 50°F shift or buffer relative to the most limiting calculated MPT curve is always adhered to (including reactor start-up, shutdown, and any operational upset events). Additionally, based on HTHA crack growth predictions and critical flaw sizing calculations, maximum operating reactor metal temperatures are limited to 625°F to minimize short-term HTHA crack growth. Based on crack growth predictions with a half-life approach for an inspection interval, crack growth at 650°F could potentially result in an existing crack-like flaw reaching critical dimensions prior to the next planned maintenance opportunity or reactor replacement. If an unexpected unit trip (shutdown) occurs, targeted follow-up inspection is recommended to benchmark any damage progression or crack growth at some of the most severely (known) damaged locations.

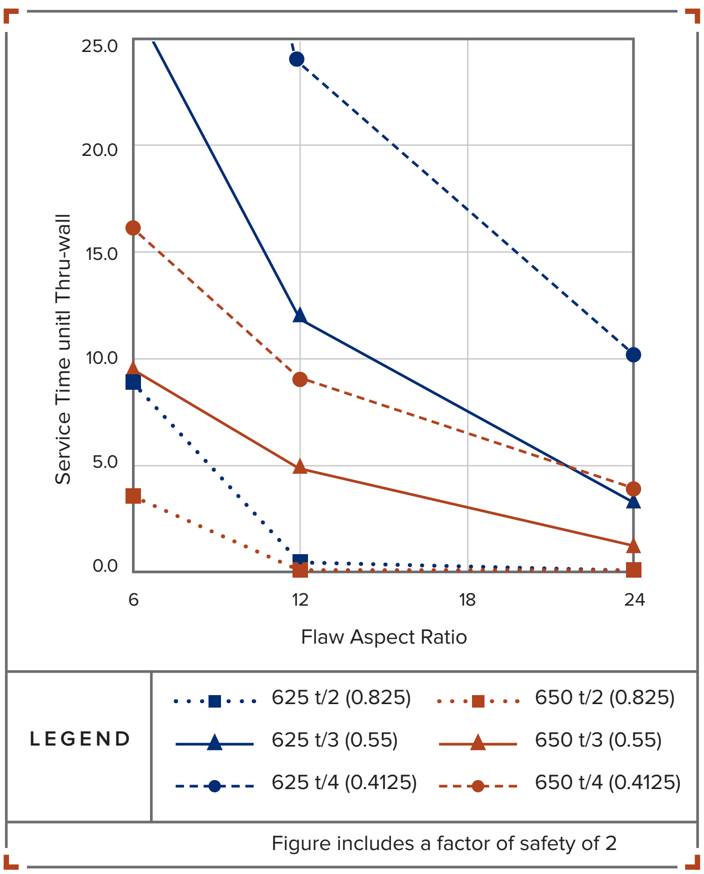


Figure 13. *Predicted Crack Growth Rates in the Cylindrical Shell*

SUMMARY AND CONCLUSIONS

This article offers background information on the mechanism of HTHA, the resistance of C-0.5Mo material to HTHA damage and fracture, and recent developments in NDE technology to accurately identify HTHA damage. Additionally, a case study of an in-service C-0.5Mo hydrotreater reactor is summarized, where modern inspection techniques identified incipient HTHA and the presence of some crack-like flaws in pressure boundary welds. Furthermore, a significant portion of historical operating points fall above the current PWHT carbon steel Nelson Curve (currently recommended for C-0.5Mo in API 941 [3]). Fracture mechanics-based MPT envelopes are generated based on this identified damage to guide pressurization procedures that mitigate the risk for brittle fracture, particularly during start-up and shutdown. Also, historical operating hydrogen partial pressure and temperature histograms are established to try and bound past operating data, and HTHA damage is evaluated based on methods developed through E²G's ongoing JIP [9-11]. Crack growth predictions are also employed to gain confidence in safe short-term operation, until planned reactor replacement can feasibly take place (an approximately two-year timeline).

Ultimately, new IOWs were established to mitigate the risk for both brittle fracture and time-dependent HTHA crack growth. External steam tracing was installed to achieve a bulk pressure boundary metal temperature of 200°F prior to reactor pressurization to avoid brittle fracture. These IOWs ensure that the proposed MPT envelope with a 50°F shift or buffer relative to the most limiting calculated MPT curve is always adhered to and that maximum operating reactor metal temperatures are limited to 625°F to minimize short-term HTHA crack growth. If an unexpected unit trip (shutdown) occurs, targeted follow-up inspection is recommended to benchmark any damage progression or crack-growth at some of the most severely (known) damaged locations. While the long-term recommendation is to replace the reactor, the analysis methods described herein and implementation of new IOWs, coupled with modern NDE techniques carried out by a fully-trained inspector, offer a means to manage the risks associated with operating this 1970s vintage hydrotreater reactor (with possible HTHA damage) in the short-term. Additional details on the case study summarized in this article are available in Reference [29].

REFERENCES

[1] Bosen, C., 1933. "Attack of Steel Under Conditions of Ammonia Synthesis". Die Chem. Fabrik, p. 127.

[2] Evans, T., 1948. "Hydrogen Attack on Carbon Steels". Mechanical Engineering, 70, pp. 414–416.

[3] API, 2016. Recommended Practice 941: Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants, 8th ed. American Petroleum Institute, Washington, DC.

[4] Lundin, C., Bharadwaj, M., Barlow, W., Barnard, B., and White, S., 2014. Welding Research Council Bulletin 548: Effect of Hydrogen Attack on the Mechanical Properties of a C-1/2Mo Steel. Welding Research Council, Inc., Shaker Heights, OH.

[5] Nelson, G., 1949. "Hydrogenation Plant Steels". In 1949 Proceedings API. Vol. 29M, pp. 163-174.

[6] API, 1967. API Publication 940, Steel Deterioration in Hydrogen (Out of Print). American Petroleum Institute, Washington, DC.

[7] API, 1975. API Publication 945, A Study of the Effects of High-temperature, High-pressure Hydrogen on Low-alloy Steels (Out of Print). American Petroleum Institute, Washington, DC.

[8] Fletcher, E., and Elsea, A., 1964. DMIC Report 202: The Effects of high-Pressure, High-Temperature Hydrogen on Steel. Defense Metals Information Center - Battelle Memorial Institute, Columbus, OH.

[9] Panzarella, C., and Cochran, J., 2015. E²G Technical Report 48: Report on the HTHA Models Used for FFS Assessments and RBI Implementations HTHA JIP Phase 1 Final Report. The Equity Engineering Group, Inc., Shaker Heights, OH.

[10] Panzarella, C., and Cochran, J., 2016. E²G Technical Report 60: Technical Background for the E²G HTHA Model. The Equity Engineering Group, Inc., Shaker Heights, OH.

[11] Osage, D., Panzarella, C., and Cochran, J., 2017. E²G Technical Report 94: E²G HTHA JIP FFS Rules for API 579-1/ ASME FFS-1, Part 15 Version 7. The Equity Engineering Group, Inc., Shaker Heights, OH.

[12] Nugent, M., Silfies, T., Dobis, J., and Armitt, T., 2017. "High Temperature Hydrogen Attack (HTHA) Modeling Prediction and Non-Intrusive Inspection Review".

[13] Prueter, P., and Nugent, M., 2019. "Fitness-for-Service Case Studies in HTHA Equipment". In 23rd International Pressure Equipment Integrity Association (IPEIA) Conference.

[14] Kowalski, P., Prueter, P., and Nugent, M., 2018. "Fitness-for-Service Case Studies in HTHA Equipment". In Paper 17-3D: AIChE Ammonia Safety Symposium.

[15] API, 2016. API 579-1/ASME FFS-1 Fitness-For-Service. The American Petroleum Institute, Washington D.C.

[16] Silfies, T., 2016. "Looking Behind the Curtain of API 941 HTHA Data". NACE International, Corrosion Conference and Expo.

[17] Nageswaran, C., 2018. Maintaining the integrity of process plant susceptible to high temperature hydrogen attack. Part 1: analysis of non-destructive testing techniques. Health and Safety Executive (HSE), London.

[18] Rothwell, J., 2018. Maintaining the integrity of process plant susceptible to high temperature hydrogen attack. Part 2: factors affecting carbon steels. Research Report RR1134 - Health and Safety Executive (HSE), London.

[19] EEMUA, 2018. Publication 240 - Factors to Consider when Managing High Temperature Hydrogen Attack on Petroleum and Chemical Facilities. The Engineering Equipment and Materials Users Association (EEMUA), London.

[20] McLaughlin, J., Krynicki, J., and Bruno, T., 2010. "Cracking of Non-PWHT'd Carbon Steel Operating at Conditions Immediately Below the Nelson Curve". In ASME Pressure Vessels and Piping Conference. PVP2010-25455.

[21] API, 1977. Recommended Practice 941: Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants, 2nd ed. American Petroleum Institute.

[22] API, 1990. Recommended Practice 941: Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants, 4th ed. American Petroleum Institute.

[23] Nugent, M., and Armitt, T., 2018. "HTHA Inspection Detection Confidence Improves Basis for New API Recommendations".

[24] ASME, 1974 Addenda. Section VIII Division 1: Rules for Construction of Pressure Vessels. American Society of Mechanical Engineers Boiler and Pressure Vessel Committee, New York, NY.

[25] Shewmon, P., and Xue, Y., 1991. "Effect of High-Pressure Hydrogen on Crack Growth in Carbon Steel". Metallurgical Transactions,22A, pp. 2703–2707.

[26] Osage, D., Spring, D., Anderson, T., Kummari, S., Prueter, P., and Wallin, K., 2017. Welding Research Council Bulletin 562: Recommendations for Establishing the Minimum Pressurization Temperature (MPT) for Equipment. Welding Research Council, Shaker Heights, OH.

[27] Prueter, P., Kummari, S., and Osage, D., 2017. "A Fracture Mechanics-Based Approach to Establish Minimum Pressurization Temperature Envelopes". In ASME Pressure Vessels and Piping Conference. PVP2017-65805.

[28] Wallin, K., 2011. Fracture Toughness of Engineering Materials. EMAS Publishing, United Kingdom.

[29] Prueter, P.E., Jones, J.R., Hess, J. and DeLuca, J., "Managing the Risks Associated with Operating a Hydrotreater Reactor with Possible High-Temperature Hydrogen Attack Damage." PVP2019-93533, Proceedings of 2019 ASME Pressure Vessels and Piping Conference, July 14-19, 2019, San Antonio, Texas.

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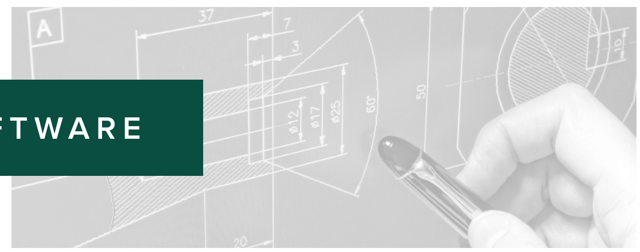

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