A PRACTICAL RESPONSE TO HTHA

Daniel Drabble, Brian Olson, Mark Carte, Zach Cater-Cyker, and David Keen, Becht, USA, explore how the ammonia industry can respond to and mitigate high temperature hydrogen attack (HTHA).

High temperature hydrogen attack (HTHA) is a damage mechanism which has been known of since before the start of the Second World War,[1] but nearly 90 years later remains a subject of debate among metallurgists, inspectors, engineers, and scientists.

Historically, the approach to design and risk mitigation has revolved around the 'Nelson curves', a set of empirically derived guidelines first published in the 1940s[2] that defined operating limits for steels exposed to high-temperature hydrogen. Later incorporated into API RP 941,[3] these curves have evolved, including removal of the C-0.5Mo line in the Fourth Edition (1990) and the introduction of a lower carbon steel curve for non-post-weld heat-treated (non-PWHT) welds in the Eighth Edition (2016). Mechanistic models of HTHA have been proposed and developed since the 1970s/80s,[4 - 9] however, it is only in the past decade or so that such models have been integrated into the assessment process for industrial equipment – an effort aimed at capturing the nuances of HTHA that the Nelson curves were never intended to explain.

So how should integrity and reliability engineers in the ammonia industry respond to the challenge of HTHA? Given all that has been learned in the last 10 - 15 years through incidents (including a particularly tragic one in 2010[10]), through intensive studies and lessons shared across multiple industries, how should the approach be evolve?

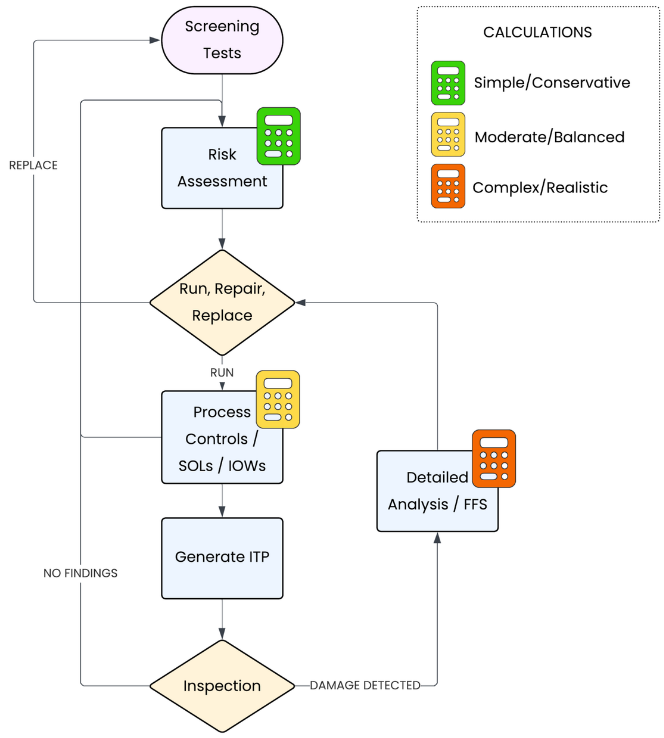

Figure 1. General approach to managing HTHA in industrial plant.

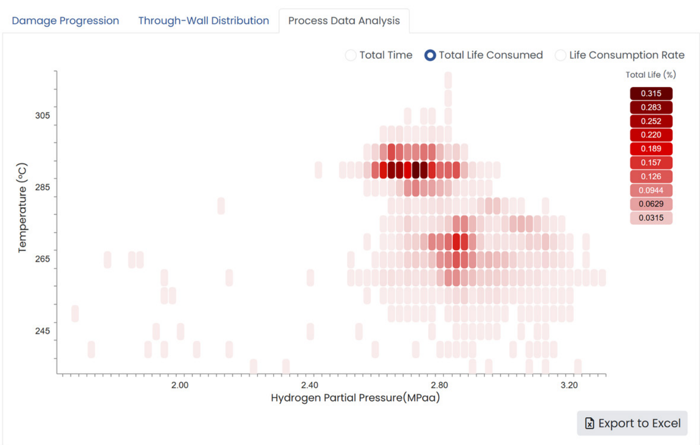

Figure 2. Example of process data 'heat map' from Becht HTHA, which demonstrates life consumption for various operating modes.

Let us briefly mention the design phase, which is relatively straightforward and primarily hinges on materials selection. The Nelson curves are specifically intended for the purposes of design, and with the upcoming Ninth Edition of API RP 941, will provide more guidance with the introduction of time-based design curves. Design is by far the most effective control, and getting it right at this stage dramatically reduces the risk throughout the equipment lifecycle.

But most of us are not in that situation. For those of us tasked with managing existing equipment, let us examine a thought process; a general approach to managing HTHA in industrial plant. This is shown in Figure 1. Each process and decision is then discussed in the following paragraphs.

Screening tests

The logical first question is: is my equipment at risk of HTHA? The ammonia producers which are most actively managing HTHA tend to be the older plants (circa 1960s/70s), often due to C-0.5Mo or non-PWHT carbon steel equipment. However, those are not the only ones. Current discussions about low-alloy steels, particularly 1Cr-0.5Mo and 1.25Cr-0.5Mo, closely mirror earlier concerns about C-0.5Mo. There have been cases of significant HTHA damage below the Nelson curve for low-alloy steels, not just in the catalytic reforming area of the refining industry but also in the ammonia industry. There have also been questions regarding the unusual shape of the Nelson curve for 1.0Cr-0.5Mo and 1.25Cr-0.5Mo at moderate hydrogen partial pressures, which ammonia producers should be interested in, as their synthesis loops operate in precisely this area of the curve.

For ammonia plants, the equipment most susceptible to HTHA typically includes:

- High-temperature (HT) shift converters.
- Ammonia converters.
- Methanators and exchangers.
- Synthesis loop piping.
- Refractory lined equipment (e.g. primary reformer transfer line or secondary reformer).
- Waste heat boilers (tubesheets and bypass lines).

Most producers have, by now, conducted some form of HTHA screening. These range from simple temperature flags (e.g., hydrogen service > 350 - 400°F) to comparisons with conservatively adjusted Nelson curves. The intent here is speed and simplicity. One warning though: do not exclude equipment from the screening analysis based solely on material grade unless that grade has been positively verified at all critical locations. In one such case, a carbon steel filler metal was found to contain HTHA fissuring in a nominally P11 piping line, illustrating the masking effect of incorrect material assumptions.

Risk assessment

Now that we have a shortlist of equipment, the next step is normally to conduct a risk assessment. Some studies evaluate time spent near or above the Nelson curves, potentially leveraging the time-based 'incubation curves' in recent editions of API RP 941. Becht's method, for example, often starts with simplified life calculations under design or conservative historical conditions, followed by sensitivity studies to refine the risk profile.

One potential outcome of a risk assessment is a decision to replace equipment even without confirmation of damage. The combination of high consequence of failure, uncertainty regarding risk controls, and high cost and complexity of inspecting and managing at-risk equipment has in some cases led straight to replacement without verifying whether HTHA was present. Few could argue: elimination of risk sits at the top of the hierarchy of controls.

More often, though, the goal is to right-size the mitigation strategy – to match inspection and maintenance efforts to the actual risk. This requires evaluating both likelihood and consequence, the latter rarely being less than severe given the potential for brittle fracture in hydrogen service.

Process controls, operating limits, and integrity operating windows

Recognising and monitoring the parameters which contribute to HTHA damage is a step that is occasionally poorly implemented or even overlooked. While many of these parameters are beyond control, temperature – and to a lesser extent, hydrogen partial pressure – are the most practical for real-time monitoring. Additional controls, such as temperature ramp-rate limits and minimum pressurisation temperatures (MPTs), are also frequently applied to hydrogen systems and likely consider related mechanisms such as hydrogen-induced cracking (HIC).

The development of integrity operating windows (IOWs) is outlined in API RP 584,[11] and HTHA is cited multiple times in the Annex with specific reference to steam-methane reformers. Historically, these limits were calculated using the Nelson curves, and no doubt they still are, although the progress of damage modelling in recent years has allowed a more refined approach. The ability to analyse substantial amounts of process data can lead to valuable insights as to which operational 'modes' are causing damage, as shown in Figure 2.

Generate the inspection test plan (ITP)

The ITP is informed by the risk assessment and revolves around two fundamental, but far from trivial, questions:

- Where, specifically, will we look?
- What surface preparation, equipment, techniques and inspectors will we use?

On the plus side, examination of assets for HTHA has evolved drastically in the past 10 years. Detecting HTHA is relatively common, and experience has shown that a pressure vessel can have HTHA and remain in operation. To date, one entity has reported detection and confirmation of HTHA damage in 32 out of 34 pressure vessels examined.

The American Petroleum Institute (API), jointly with industry experts' contributions, has provided a detailed non-destructive testing (NDT) protocol for examination of assets for detection of HTHA. The current edition of API RP 941,[12] in Section 6 and Annex E, has valuable information detailing the various NDT techniques, including guidance on the detection limits, sizing, advantages, and limitations of each. Currently favoured is a combination of time of flight diffraction (TOFD), phased-array UT (PAUT) and full matrix capture/total focusing method (FMC/TFM). If we have internal access, high-sensitivity wet fluorescent magnetic particle testing (HSWFMT) is a highly worthwhile addition to specify up front, as well as a careful visual inspection. The reality is that no technique is perfect, so use of supporting and complementary methods are important for confidence in results. Note the information pertaining to HTHA examinations within API 941 has been expanded and now resides in API 586 which will be published mid-year 2025.

Inspection

If there are no findings from the planned inspection, then we should update our risk assessment. However, do remember that 'no findings' does not necessarily mean 'no damage'. It can be a useful exercise to assume the worst, i.e. that HTHA damage does exist at the limit of detection, and then to extrapolate that into the future. Becht performs this analysis regularly in order to justify future inspection intervals, as demonstrated in Figure 3.

If ultrasonic inspection reveals possible indications, it is wise to follow up with other techniques.
As mentioned, HSWFMT is very good at detecting HTHA damage on the internal surface. Similarly, replication can be useful and also provides information about the microstructure, although this can be biased by the presence or absence of decarburisation, which is no longer considered a definitive indicator of HTHA. Importantly however, these techniques are limited to only revealing

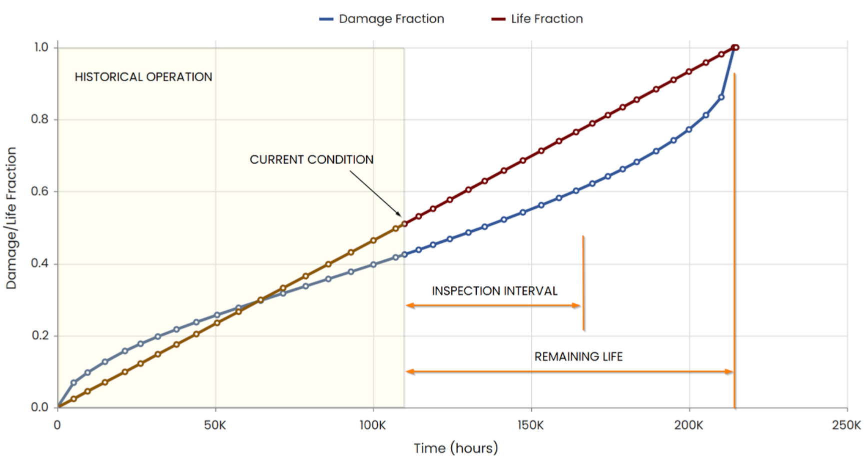

Figure 3. Illustration of concept of calculating future inspection intervals from known or assumed current condition.

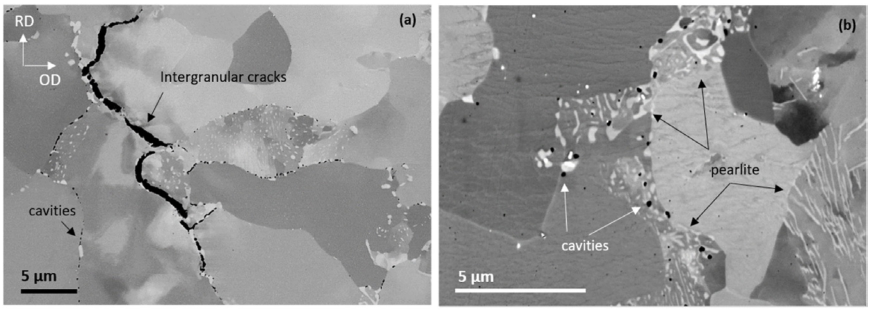

Figure 4. HTHA damage in a C-0.5Mo hydrofinishing reactor. Figure modified from '3D FIB-SEM and TEM Characterization of an Industrial 0.5-Mo Low Carbon Steel Affected by High-Temperature Hydrogen Attack' by Flament et. al., 2024, International Journal of Hydrogen Energy (CC BY 4.0). Image has been cropped.

the condition of the surface. Much better is metal removal (scoop or boat samples), which in many cases can be performed without requiring repair by conducting (beforehand) a separate locally thin area (LTA) analysis. These samples offer us an important ability to understand not just the damage 'stage', but also allow us to validate UT sizing efforts and understand the variation as a function of depth which is sometimes lost in our damage classification systems.

Optical micrography is useful, but do heed the warnings given in API RP 941 regarding the potential for etching to obscure damage. In Becht's experience, there really is no substitute for scanning electron microscope (SEM) analysis. SEM is able to consistently detect very early-stage damage which gives confidence that we are getting an accurate picture of the current material condition at various depths. For example, see the individual cavities which can be resolved in Figure 4, reproduced from recent work by Flament et al.[13]

If the inspection findings are ambiguous, especially when there is no access to the internal surface, ask yourself whether HTHA is really the likely mechanism. UT alone often cannot definitively answer this question, but a combination of UT and damage modelling has in the past been able to show that HTHA is not particularly credible, and regardless would not be expected to propagate. Similarly, a repeat inspection with improved surface preparation has also resulted in significant reclassification of results.

If damage is confirmed and believed to be HTHA, there are options. 10 years ago, it would have been difficult to justify returning to service; the appearance of early-stage damage has been known to condemn equipment, prevent restart, or drastically limit subsequent run lengths. Today, in addition to improved inspection techniques, damage models are available to extrapolate from current condition out to end-of-life, effectively generating a remaining life in the same way that we are used to with, for example, an API-579[14] Part 10 creep calculation. We can incorporate process data directly, run sensitivity analysis on certain parameters, consider both 'volumetric' and 'crack-like' morphologies (HTHA manifests as both), and incorporate appropriate levels of conservatism in the same way we would with a creep analysis. Such analysis can be used to justify continued operation, to set future inspection intervals, to calculate IOWs or for CAPEX planning.

In fact, as may have been apparent from the flowchart presented back in Figure 1, damage modelling plays a valuable role throughout the HTHA management process, from initial screening and risk assessment, to the definition of operational limits, through to the evaluation of the end of useful life. The real advancement in the last decade or so, however, has been the convergence of improved modelling and inspection methodology. Better inspections have informed better models, and better models have refined our inspection focus. The result is a more powerful, integrated approach; the whole is indeed greater than the sum of its parts.

As an industry, we must remain vigilant about HTHA. We cannot claim to have all the answers, and the risk of complacency remains real. But it is encouraging to see progress in our collective response. WF

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