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A NEW METHOD FOR PRIORITIZING EQUIPMENT IN HTHA SERVICE FOR INSPECTION AND REPLACEMENT

and the Challenges in Obtaining Process Conditions to be Used in the HTHA Assessment

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High Temperature Hydrogen Attack (HTHA) is a complex damage mechanism that continues to defy investigators trying to make predictions on the anticipated degree of damage or service life. This article provides some background on HTHA, discusses some current developments in HTHA inspection and mitigation, and describes how one Refiner is instituting an HTHA risk management plan for its refineries and the challenges and pitfalls they have encountered. The article also describes a new innovative screening methodology developed by the author, who served as the Corrosion & Materials Engineering expert assisting the Refiner in characterizing over 75 equipment items operating in high temperature hydrogen services that needed individualized risk management plans. Materials included in the evaluations are carbon steel (CS), C-0.5Mo, 1Cr, and 1.25Cr equipment ranging in service exposure of 10 to over 50+ years. Several examples are provided.

WHAT IS HTHA?

Mechanistically, HTHA can be thought of as hydrogen promoted creep damage at temperatures below the typical creep regime. Atomic hydrogen present in the process environment must first enter the surface of the equipment and then can diffuse into the subsurface. Atomic hydrogen combines with carbon present in unstable carbides to form methane. At first this creates very small bubbles, and then as the pressure in the bubbles builds, they begin to combine to form fissures, and these fissures then combine to form cracks.

BACKGROUND

The historical method by which the industry has managed HTHA has been to use experienced-based curves (API 941 Nelson Curves) that were drawn below the lowest reported case of HTHA attack. Generally speaking, these curves have been used for material selection and for evaluating the integrity of existing equipment, and have served the industry well. The Nelson Curves show a temperature/pp H₂ (hydrogen partial pressure) relationship for each material.

Although the shape of the Nelson Curve for CS is experientially based, the API TR 941 Technical Basis Document (TBD) describes the theoretical basis for the Nelson Curves based on first principles and confirms that their general shape and position in P/T/Material (pressure/temperature/Material) space is fundamentally sound. Thermodynamically, the methane formation reaction is favored at the lower the temperature, but the reaction rate becomes limiting at lower temperatures. Therefore HTHA is more

likely to occur at intermediate temperatures which coincides with engineering use of the common materials of construction. It has long been known that alloy additions of Cr (chromium) and Mo (molybdenum) create more stable carbides than the iron carbides in carbon steel and will not form methane as readily.

In reality, HTHA is much more complicated and there are many other factors such as age, upsets, stress, PWHT, etc. that determine an actual materials' particular susceptibility or resistance to HTHA.

CURRENT INDUSTRY ISSUES AND CHANGES TO THE NELSON CURVE

Because the Nelson Curves are experienced-based, material curves have been adjusted or material curves were removed as experience with HTHA was developed. Specifically, the C-0.5 Mo curves were adjusted downward in the 1980's and later the material was removed altogether from API 941 for new equipment (API 941 4th Edition 1992). In 2010 Tesoro Anacortes NHT unit experienced a failure in a non-PWHT'd carbon steel (CS) exchanger shell with multiple losses of life. The investigation showed that HTHA was the cause and both the US Chemical Safety Board (CSB) and Tesoro believe that the exchanger operated below the CS Nelson Curve. Since the Tesoro failure there have been other reports of CS experiencing attack below the CS curve (all cases were not PWHT'd) and these cases will be documented in the new 8th Edition of API 941 that should be issued in 2015. This has led to a draft proposal by the API 941 task group to lower the CS curve for welded but not-PWHT'd steel. The existing 7th Edition CS curve remains at its current location and will be renamed, base metal or welded and PWHT'd carbon steel. The CSB has urged that API 941 adopt a position that CS not be used above 400F. So far the industry has resisted that suggestion. The exact position of the new (lowered) CS non-PWHT curve is being set as part of the current API 941 balloting, but is lower than the current CS curve minus 50F in the knee region, because of two HTHA damage points submitted by Marathon Petroleum.

Industry Response:

Given that both CS and C-0.5Mo equipment are now deemed more likely to suffer from HTHA, the industry has been examining/screening their equipment for HTHA damage. In many cases, operators have replaced piping with higher resistant low Cr alloys, but heavier wall vessels like heat exchangers and reactors have often continued to be operated. The biggest challenge is that all equipment operating conditions vary over time and to

decide what conditions will be used to evaluate the equipment is a difficult task. If conservative assumptions are made for all aspects, then a large number of equipment items will not pass a simple screen. Inspecting and finding HTHA damage with NDE is also very challenging, due to the nature of the damage and microscopic evaluation.

Unfortunately, HTHA evaluation tools are very limited. The API RP 941 really does not cover risk assessment of existing equipment well and the 941 Technical Basis Document (TBD) tried to identify remaining life/FFS methods, but concluded that these were just not practical and further development work was needed. API RP 581 (API RBI) method is very simplistic and has been discredited by some in the industry. API 579-1/ASME FFS-1 2007 Edition does not contain a section on HTHA and the new version due to be published in 2015 also does not contain a section on HTHA. One simplified method that was developed and applied at ExxonMobil was published by Jim McLaughlin. Another method using samples removed from the OD and then subjected to accelerated testing to determine some level of susceptibility was developed by Tim Munsterman. Brian Olson of Stress Engineering presented a promising, further developed methane pressure model at the API 941 session at the Fall 2014 NACE/API meeting.

REFINING COMPANY PROJECT

In the following study, a North American Refiner (ANAR) decided to institute a targeted HTHA risk management plan. ANAR, as have all major refiners in the US, has had to deal with C-0.5Mo equipment that is still operating above the CS curve decades after the curve was removed from API 941. With the recent industry failures of non-PWHT'd welded CS and a concern for some very old 1Cr reactors, ANAR put together a very broad list of equipment that could be susceptible to HTHA using design pressure as hydrogen partial pressure and maximum believed temperature, and this generated a list of over 80 items across multiple ANAR refineries.

At that point, ANAR felt they needed an approach to characterize all of this equipment, identify the highest potential likelihood for failure (almost all HTHA susceptible equipment has a high consequence associated with it, due to the nature of the fluids processed), and then create management plans. Activities could range from inspection, IOW (integrity operating window) controls of operating conditions, chemistry to refine the analysis, or replacement on a shutdown cycle timeline or in an expedited fashion.

Pono HTHA Evaluation Method

Over the course of my career, I have had extensive experience with HTHA failures. I was an API 941 task group member for many years and was the official archive minder for API 941. I have also been a non-testifying litigation consultant on several HTHA failures. My knowledge and experience with HTHA led me to develop a new practical methodology for managing this insidious condition: the "Pono HTHA Evaluation Method".

In developing this new methodology, I considered many of the relevant factors and concluded that many more need to be considered when estimating HTHA susceptibility than just P and

T. I needed a method to consistently evaluate equipment and present results that would be easily understood by the industry. Having conducted many brittle fracture screening projects per API 579 Part 3, I felt that there were parallels that could be applied to HTHA screening, and that formed the basis for the Pono HTHA screening.

API 579-1/ASME FFS-1 Part 3 handles brittle fracture screening by comparing the driving force for brittle fracture (BF) versus the material's inherent resistance to BF. Two quantities are compared: the driving force is the critical exposure temperature (CET) and the resistance, termed the (minimum allowable temperature) or MAT. The material is acceptable as long as the MAT is always below the CET.

The Pono method uses the same driving force and resistance concept for HTHA screening. However, with HTHA there is no absolute go/no-go criterion, but the difference of the two quantities determines the estimated likelihood level for HTHA to occur and the resultant recommended actions. The driving force for HTHA is defined as HTHA Temperature and Pressure (HTP) for HTHA to occur and the resistance of the steel to HTHA is defined as the Minimum HTHA resistance (MHR).

Driving Force for HTHA are the Operating Conditions

In order to estimate the driving force for HTHA, the starting point is the typical operating temperature and partial pressure of hydrogen (ppH₂). Arriving at the estimated temperature and ppH₂ is never easy, but the Pono method recommends using the mean +1 sigma or the mean +2/3*(max-mean), with shutdown or missing data subtracted out so as not to lower the mean. These conditions are then adjusted based on a number of the following factors:

- Cladding type and thickness of the cladding and base metal (this lowers the HTP)
- Corrosion Scale and Fouling (this lowers HTP)
- Overall thickness - thin equipment has higher gradients than thick equipment (this lowers HTP)
- Presence of Catalyst (this raises the HTP)
- Effect of atypical operation hours and conditions (regens, power failures, etc.) (this raises the HTP)
- Confidence in operating condition data for recent and distant past (raises HTP if not highly confident, this is determined based on interviews with ops/process at each refinery). (see more later)

Specific adjustment factors in Deg. F/psi H₂ are documented in the methodology and are provided to the client as part of the report package, but the exact values are considered proprietary in regards to this publication.

This adjusted Temp/ppH₂ (HTP) is then plotted on a temperature-vs ppH₂ plot.

Table 1. Risk Management Table (These are starting points ANAR adopted, however these can be customized based on specific refinery constraints. A different corporate risk matrix could be used and adopted.)

HPT vs MHR	Likelihood Category	Replace Mitigate/Evaluate uateu	Inspect
HPT < MHR - 50	Extremely Low	No	Yes, once every 10 years
HPT < MHR - 25	Very Low	No	Yes, once every 5 years
HPT within +/-25 of MHR	Low	Yes within 5 years	As soon as possible
HPT > MHR + 25	Moderate	Yes Next shutdown or within 2 years	Online TOFD
HPT > MHR + 50	Moderately High	Immediately (within 6 months)	Online TOFD

Material Resistance Base Materials Characteristics

In order to estimate the materials resistance to HTHA, the starting point are the standard Nelson Curves (API 941 7th Edition for CS, 1Cr, 1.25Cr and a 50F/50 psi offset above the CS curve for C-0.5Mo. For Mn-0.5 Mo steel, the last published C-0.5 Mo curve in the 4th Edition of API 941 is used. For 0.5Cr-0.5Mo a curve was invented and placed about 1/3rd of difference of the distance between the a C-0.5Mo and 1 Cr curve, above the C-0.5Mo curve). These curves are then adjusted based on a number of the following factors:

- PWHT or not (non PWHT lowers it)
- Membrane Stress Level (low stresses raise curve)
- Age (The API 941 curves are set at time = X, where X varies with materials, e.g. for CS X =200k hrs., for C-0.5 Mo X= 400,000hrs. etc. continuing exposure time (age) lowers the curve)
- Chemistry factors (Mo or Cr to C ratios and elements like P, S, etc.)
- Steel Quality (Chemistry) and HTHA inspections conducted (frequency, methods, and zones). Effective inspection raises the curve or no inspection lowers the curve.

Specific adjustment factors in Deg. F/psi H₂ are documented in the methodology and are provided to the client as part of the report package, but the exact values are considered proprietary in regards to this publication. Everything is documented in spreadsheets and they can be used for “what if” analysis in the future. The original material curve and the adjusted material curve (MHR curve) are then plotted. The relative position of the HPT and MHR determine the likelihood category. Several examples of the resulting curves are included in **Figures 1-6**.

Risk Management

All HTHA services are assumed to have a relatively high consequence, so the differentiator is likelihood. Five levels of likelihood are defined in relation to the difference between the HPT and MHR curve. The industry experience has shown that very few failures have occurred in relation to the numbers of equipment components operating in potentially HTHA damaging service. Suggested actions such as inspection, replacement, and/or mitigation activities (such as setting IOW's or installing a refractory lining to lower the temperature) and their timing depend on the likelihood category according to **Table 1**.

A “what-if” check is done to determine the difference in 10 years or two shutdown cycles in the future to ensure that recommended actions keep the equipment in the same or lower

likelihood category.

Overall Project Assessment

It is extremely important to obtain accurate process operating history from the refinery. This can be challenging particularly for data from pre DCS (digital control system) days. Most equipment evaluated has 30 to 50 years of service under its belt and has encountered varying conditions; and often the conditions and the upsets are just not known. Therefore a greater safety factor is added to equipment for which the ops/process experts are unsure about past operations. This method also heavily penalizes frequent runaways, overheats, alternative conditions to assess the likelihood level. It has not been shown that Robinson's rule (life fraction approach) is valid for HTHA as is commonly used for creep, because an upset may activate damage not normally occurring and then could continue to damage below a threshold. The results so far appear to make sense and customized plans (IOWs) are being implemented.

Obtaining all of the data needed even for this simple practical approach is considerable and challenging to get refinery teams together to discuss the process conditions. In the ANAR project, the names of the people providing the process data are documented in the reports. Any prediction method, even if it has a more robust theoretical model, will suffer from the same complication of data accuracy and estimation for past service exposure.

For the equipment analyzed, there has been a good distribution of likelihood in the extremely low to low categories with a few moderate likelihood category items discovered. Action plans are being implemented and ANAR feels this approach is practical, doable, and helps prioritize the equipment for risk management activities and possible eventual replacement.

Validation

Several examples of failure points were run through the method and if some of the conservative boundary conditions are assumed, (this type of data was not usually reported so it was challenging to get a one to one comparison), the Pono method appears to predict damage or no damage as represented by API 941 data. This method considers many more factors than any traditional or complex model and presents the data in a practical graphical method that is easy for an inspector or plant engineer to understand.

CONCLUSION

The Pono method is a simple to use approach utilizing familiar results presentation concepts such as the operating conditions and a “Nelson Curve”. In this method, both the plot point and the material resistance curve are adjusted based on a number of

