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# PRACTICAL HTHA EXPERIENCE AND TIME-BASED NELSON CURVES FOR IMPROVED EQUIPMENT LIFE MANAGEMENT

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## ABSTRACT

High temperature hydrogen attack (HTHA) has been a known failure mechanism for many years, with the Nelson Curves (ref. API RP 941) being almost 60 years old. While research and industry learning has been ongoing, failures below the Nelson Curves for non-post weld heat treated carbon steel (CS) have occurred in the last 10 years, and as such, the learning continues. These more recent failures have spurred multiple joint industry projects that are still ongoing. While we believe testing is extremely valuable, and look forward to continually testing our models as new information becomes available, we also believe that there are contributions that can be made right now. The gap is not in HTHA's critical factors, which are well understood by material experts, nor is it in the technical feasibility of the Nelson Curves that has been repeatedly demonstrated (ref. API TR 941-A). Rather, the biggest gaps are:

1. relating time to failure,
2. incorporating varying operation data, and
3. treatment of welds.

This article stands on the shoulder of giants to tie the Nelson Curves, which are the foundation of our industry's HTHA programs, to mechanistic models from several sources that will allow us to recreate Nelson curves for different operational histories and time durations. By using this work, married with the recent advances in nondestructive examination (NDE) (e.g., new API 941 Appendix E guidelines) we believe that managing equipment with damage is now both possible and reasonable.

## INTRODUCTION

Becht published an article discussing our Pono screening method for HTHA ("Pono HTHA Evaluation Method") over five years ago in *Inspectioneering Journal*,<sup>[1]</sup> with the goal of handling the gaps in the Nelson Curves<sup>[2]</sup> from a high-level perspective. This method incorporated known critical factors such as exposure time, steel chemistry/quality, confidence in operating conditions, upsets, and operating stress levels to provide owner-operators with a higher confidence screening method.

Our goal with this article is to continue giving owner-operators higher confidence by extending our practical method to be more quantitative/less empirical. We do this by taking the results of decades of development on void growth and using them to produce the standard Nelson Curve. In our experience, the data and models essentially taken directly from the literature do this

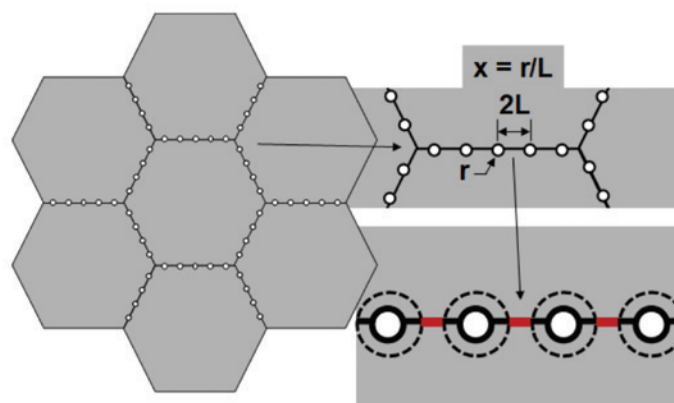


Figure 1. Idealized Void Growth Models

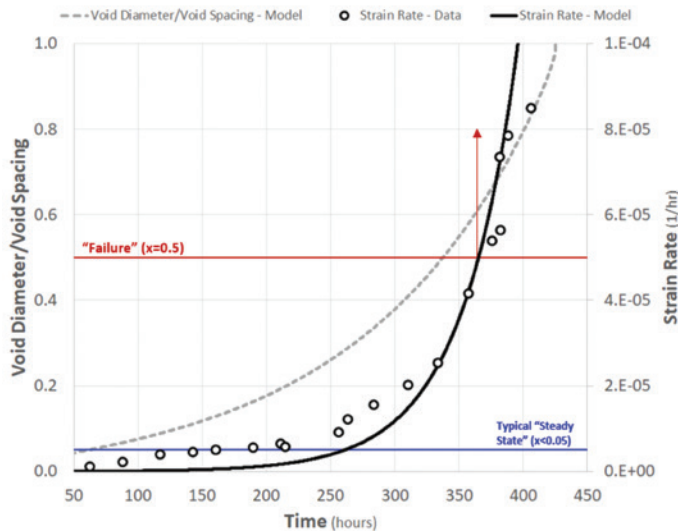
remarkably well for the carbon steel (CS) test case presented here. The benefits of describing the Nelson Curves with an analytical model vs. curve fitting (as the Pono Method did previously) are large; time is explicitly a part of the model and critical factors such as external stress and metallurgical factors can be directly incorporated.

## FAILURE CRITERION AND BACKGROUND

HTHA damage is similar in nature to creep damage and HTHA makes liberal use of creep concepts and models.<sup>[2]-[17]</sup> Voids initiate, grow, and coalesce on susceptible grain boundaries, which is illustrated in **Figure 1**. Models for void growth have been around for some time, and these same basic models are used here. In all cases, there are two physical mechanisms of void growth – the first is diffusion where stress normal to the grain boundary sets up a loop in which iron atoms from around the void are deposited on the adjacent grain boundary, thickening it and pushing the grains apart. This separation and the loss of iron atoms cause the void to grow. Perhaps even more unintuitive is that this mechanism dominates only at high (traditional creep) temperatures. Even at temperatures where we think of creep as negligible, it is in fact creep very local to the voids that leads to damage. Why this happens is discussed in the next section.

While void growth models have existed for decades, it wasn't until Sagüés et. al. added creep to the model<sup>[4]</sup> and Johnson and Shih had the idea that at some point the ligaments would be overloaded. By introducing a failure criteria for the ligaments, the void growth models were then tied directly to the Nelson Curve.<sup>[9]</sup> This idea is also illustrated in **Figure 1** where the red lines depict the ligaments at overload. HTHA uses the idea of normalized void radius





**Figure 2.** Strain Rate versus Time Validation

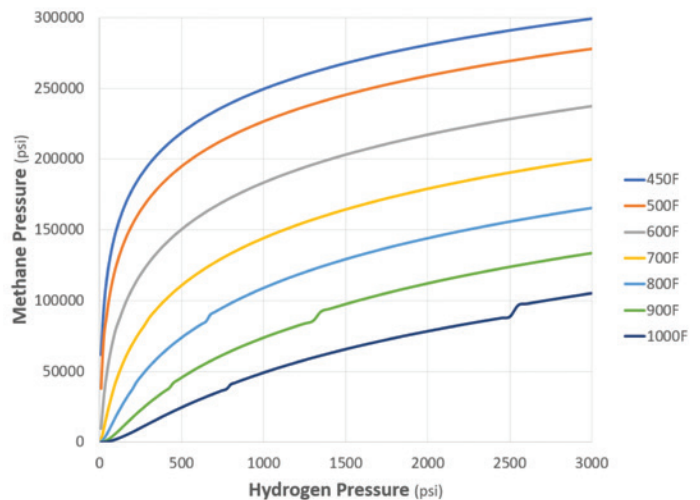
(diameter divided by ligament) denoted  $x$ , and when  $x$  equals 1, the voids would touch (no longer any ligament). However, the ligament would be overloaded before this, and so, a critical  $x$  (or damage) value of less than 1 is always used. Because the physics and math are so similar between creep and HTHA, it turns out that a plot of strain rate or even void radius (or  $x$ ) versus time look a lot like a creep curve. This is illustrated in **Figure 2** where the strain rate takes off after about  $x = 0.5$ , much like in tertiary creep.

While the idea of the ligaments being overloaded and failing was a simple and powerful idea, what is even more remarkable is how well Nelson-type curves shown in the Shih and Johnson paper matched the shape of the actual Nelson Curves. Maybe this shouldn't be surprising based on all the ways the shape and rough position of the API 941 Nelson Curve have been validated,<sup>[17]</sup> but it seemed a natural starting point for our work focused on capturing the data and knowledge that the API 941 Nelson Curves represent. It should be explained that the Nelson curves are created from known failures. While there appear to be trends, there is still room for improvement in understanding the parameters that lead to damage. The mental challenge is not to let the cost of capital expenditures bias us in understanding and establishing the models to justify leaving equipment in service at the cost of failure.

Another challenge is that metallurgical engineering modeling must direct where NDE inspections should be performed and provide the criteria for evaluating the results of the inspections and the degree of uncertainty in the remaining life prediction of the equipment to be fed into the models. This must include understanding the degree of uncertainty in the prediction. It must also be understood that HTHA damage can be highly localized, which poses another challenge to the engineer providing the exact locations for NDE, of course with some conservatism.

### HTHA DRIVING FORCE

HTHA can occur over a wide range of temperatures, but most concerns—and failures—have occurred at surprisingly low temperatures for CS, at least from a traditional creep perspective. This can be explained by looking at methane pressures, which



**Figure 3.** Methane Pressure Model for CS

are a primary driving force in HTHA damage. As carbon from unstable carbides reacts with hydrogen in the metal, methane is formed and trapped. The predicted methane pressures can be extreme, which is demonstrated in **Figure 3** (generated from what is now the standard methane pressure model of Odette and Vagarali<sup>[18]</sup>). As an example, a hydrogen ( $H_2$ ) partial pressure of 500 psi at 5000F gives an equilibrium methane ( $CH_4$ ) pressure of 195,000 psi – an increase of 390 times! Interestingly, the methane pressure is dramatically worse at lower temperatures, and even though these equilibrium values may not be reached in practice at the lowest temperatures, the values are still enormous. Even at the lowest traditional creep temperature for CS (from a pressure vessel design standpoint) of 7000F, that same 500 psi of hydrogen still causes a methane pressure of over 110 ksi. Compare this to the 7000F allowable stress for ASTM SA-516 Grade 70 at 7000F of 18.1 ksi and it's perhaps not so surprising that this methane pressure (6 times the allowable!) causes severe damage, even at lower temperatures.

An additional benefit of breaking out the damage mechanisms of diffusion and creep separately is that external loads can be easily incorporated consistently. For example, since diffusion is driven by the normal stress, the maximum principal stress due to external loads is used. On the other hand, since creep is driven by pressure inside the void, the "pressure" stress (average of all the principals) is used instead. While this effort focuses on lower and intermediate temperatures, traditional high temperature creep can also be included, which requires external stress to drive damage. External stresses have no perceptible impact for intermediate and low temperatures (less than 7000F, where methane pressure dominates), but do become dominant at higher temperatures (where methane pressure increasingly becomes negligible). While inclusion of external stress and high temperature creep of the bulk material predicts a maximum use temperature that varies as a function of target lifetime (and which may in fact be physical), the most meaningful predictions require simultaneous consideration of (beneficial) constraint due to undamaged material. That is, undamaged material effectively clamps down

$$\frac{dv}{dt} = 2\pi \frac{(D_b \delta_b)_o \exp\left(-\frac{Q_b}{R_g \cdot T_{abs}}\right) \Omega}{k \cdot T_{abs}} \frac{1-x^2}{x^2 \left(1 - \frac{x^2}{4}\right) - \frac{3}{4} - \ln(x)} (P_{CH_4}) + 2\pi (x \cdot L)^3 \frac{(D_v)_o \exp\left(-\frac{Q_v}{R_g \cdot T_{abs}}\right) A \cdot b \cdot \mu}{k \cdot T_{abs}} \left(\frac{3}{2n} \frac{P_{CH_4}}{\mu}\right)^n$$

the damaged material inhibiting void growth. These topics are beyond the scope of this article, but it is not unreasonable that these effects (high temperature creep due to external stress and beneficial constraint) might offset each other as the existing Nelson curves would seem to predict.

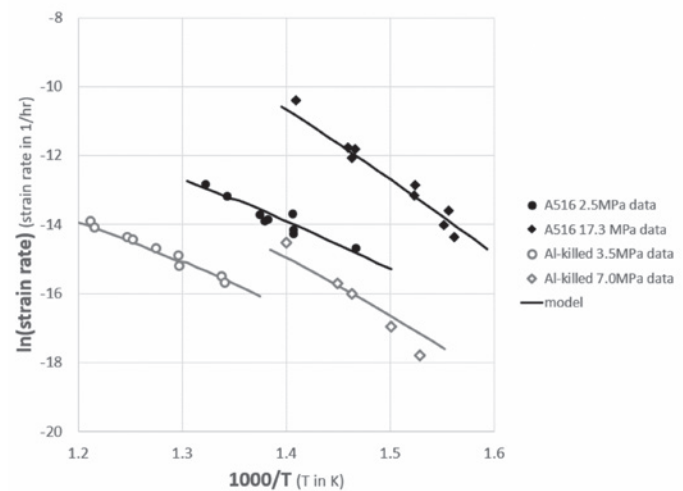
## NELSON CURVE GENERATION AND MODEL VALIDATION

The basic model used here for void growth rate ( $dv/dt$ ) is shown above.

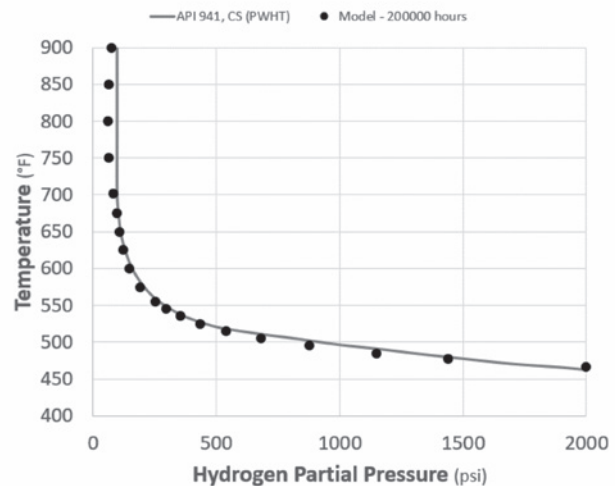
Where the first term is for grain boundary diffusion and the second is for power law creep of an infinitely thick sphere. This equation is directly from Sagüés<sup>[4]</sup> except that the power law creep constant has been updated to match more current treatment of Johnson and Shih.<sup>[9]</sup> Surface diffusion has been neglected in the above for simplicity since it has a relatively minor effect (and would take almost half a page to describe!), though it is included in all results presented (with the equation taken directly from Non-Equilibrium Models for Diffusive Cavitation of Grain Boundaries<sup>[11]</sup>). While the above equation may be “basic”, it has an intimidating number of variables at first glance. In reality, the vast majority have physical meaning and are already specified. There is a diffusion “strength” –  $(D_b \delta_b)_o$  and  $Q_b$  – and a creep “strength” –  $(D_v)_o$  and  $Q_v$  – that need to be assigned, but these variables also have physical bounds, and values are taken directly from the literature (reference Mechanisms of Hydrogen Attack of Carbon and 2¼Cr-1Mo Steels<sup>[10]</sup> for all diffusion quantities and reference A Model Calculation of the Nelson Curves for Hydrogen Attack<sup>[9]</sup> for all creep quantities). The next step is calibration, with the only free variables being the void (half-) spacing,  $L$ , and the critical ligament value for failure (which has already been set at  $x = 0.5$  per **Figure 2**). Because the models used are for unconstrained void growth, the constraint effect that undamaged material has on adjacent damaged material is essentially captured in the calibration. The calibration was performed here to simultaneously give:

- the best fit to strain rate-time HTHA data (see **Figure 2**),
- the strain rate vs. temperature and pressure data (see **Figure 4**), and
- finally the Nelson curve itself shown in **Figure 5**.

The strain rate vs. time and strain rate vs. temperature and pressure results use the typical approximate relationship between local void growth and bulk strain rate<sup>[10]</sup> which tends to underpredict strain rate (as in **Figure 2** at early times), but not unreasonably so. The strain rates shown in **Figure 4** use similar parameters as those documented in Mechanisms of Hydrogen Attack of Carbon and 2¼Cr-1Mo Steels, as would be expected since identical model inputs are used for everything but creep.



**Figure 4.** Steady State Strain Rate Validation



**Figure 5.** Model versus Actual Nelson Curve for Carbon Steel (PWHT)

The most important calibration and benchmark are to the Nelson Curve itself; with failure taken as  $x = 0.5$  (see **Figure 2**), the time was iterated until the fit shown in **Figure 5** was achieved. As shown in the figure, a time of 200,000 hours gives a close match to the actual Nelson Curve, which is very much in line with our experience and was the value for CS set in the original Pono HTHA Evaluation Method.<sup>[1]</sup> The slightly conservative results (which are maximum at 800°F) in the vertical leg of the curve are due to grain boundary diffusion and a relatively modest adjustment to the diffusion coefficient would give an extremely close fit to the entire curve. However, this minor conservatism is considered reasonable, and no values are adjusted from the published ones for simplicity. Note that the presented curve uses a linear variation between high void density ( $\approx 1012 \text{ m}^{-2}$  or  $\approx 0.55 \mu\text{m}$  spacing) at lower temperatures and lower void density at the highest

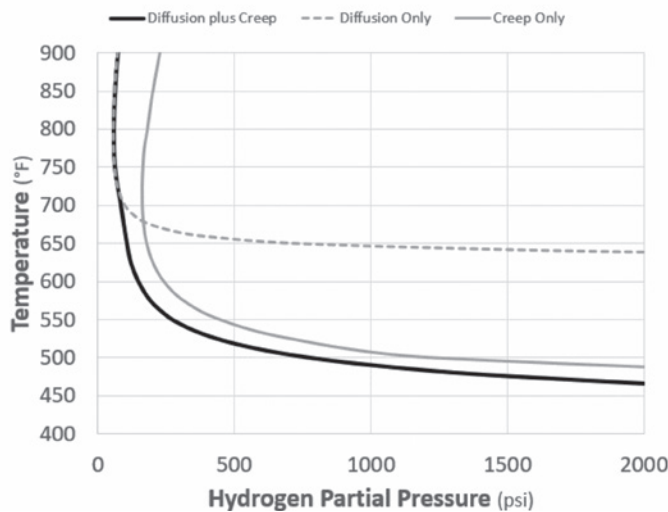


Figure 6. Model Nelson Curve for Carbon Steel (PWHT) – By Mechanism

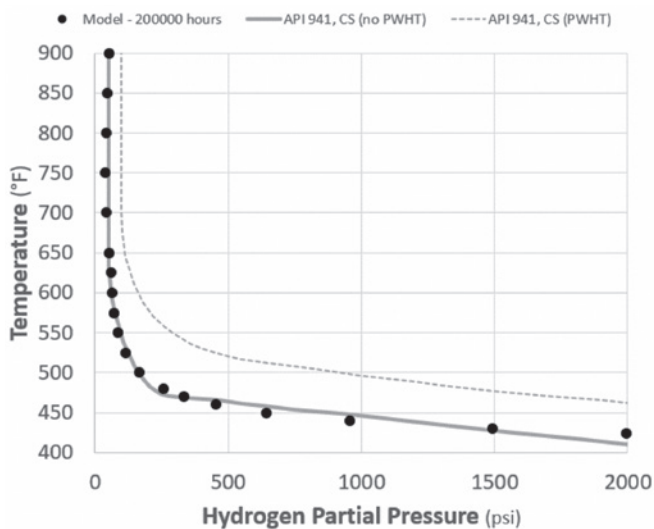


Figure 7. Model Example Time-Based Nelson Curves for Carbon Steel Welds (NO PWHT)

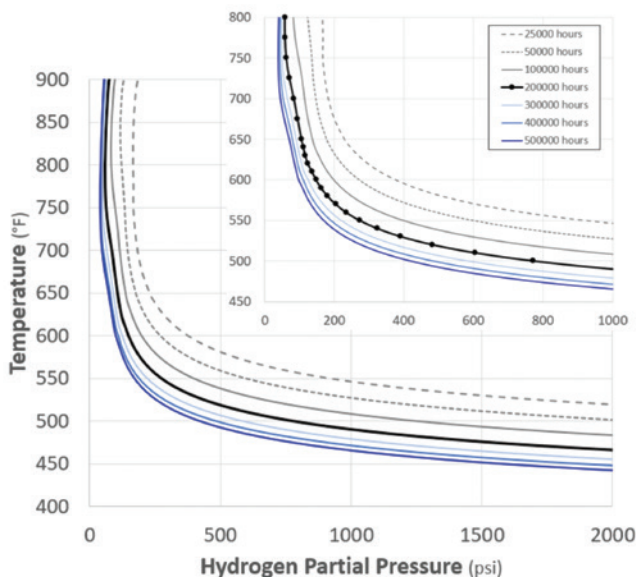


Figure 8. Time-Based Nelson Curves for Carbon Steel (PWHT) using current model

temperatures ( $\approx 1010 \text{ m}^{-2}$  or  $\approx 5.5 \text{ } \mu\text{m}$  spacing), which is in line with observed void density behavior. Therefore, really just the time was iterated to provide the best fit.

Figure 6 shows how the individual mechanisms contribute to the overall curve, and as mentioned earlier, it is really “creep” that dominates most of the curve. This is one of the reasons we believe use of the existing Nelson Curves to anchor any model is so important; there simply aren’t experiments at these relatively low temperatures and extreme pressures to fine-tune the model. Higher temperature (accelerated) testing will only give information about the higher temperature regime, which is a completely different mechanism, and as Figure 6 shows, will never predict the lower temperature failure. In fact, stresses are so high in this regime, traditional creep laws are even questionable and concepts such as power law breakdown and different diffusion mechanisms may need to be considered. Although it turned out to be a relatively small effect, an effective diffusivity<sup>[14]</sup> model was incorporated here and gives a first estimate at power law breakdown and the accelerated creep rates that can occur at intermediate temperatures and very high stresses.

Finally, Figure 2 and Figure 5 illustrate the versatility of the above model/equation. It can be integrated through time for either constant or variable conditions to track void growth (and therefore damage) the whole way (as was done to generate Figure 6). Or, the equation can be solved for temperature-pressure combinations that give a certain failure time (as was done to generate Figure 5). This versatility allows common cases to be pre-solved for convenience, as well as unique and complex cases to be solved as a time-history; for example, the effect of a higher temperature upset on hydrogen penetration and subsequent methane generation.

As a final test, the model was applied to welds. It’s assumed that the weld would cause:

1. Yield level weld residual stress
2. Increased void density (similar to cold work effect on HTHA)
3. Possibly reduced creep strength (metallurgical difference)

Results using a void density increase of 1.25x and a slightly reduced creep strength (95% of base metal activation energy) give the results shown in Figure 7. Note that this is without even including WRS which has little effect at low temperature (high methane pressures) and would tend to relax (in some cases quite rapidly) at the higher temperatures. In any case, the agreement is excellent and shows that simple, physically-based adjustments can give expected results consistent with industry experience.

While the previous discussion establishes a sound baseline, the ultimate intent of this study was to quantitatively incorporate a time basis for the Nelson curves to give owner-operators more effective/accurate tools for quantifying the risk of their in-service equipment. Time-based Nelson curves in 100,000 increments are shown in Figure 8. While direct validation of these results is largely not possible, the preceding validation gives confidence to their reasonableness and the positions are consistent with our

experienced knowledge set and what the Pono Method has been using for the past six years. Now, with the revised Pono Method using this mechanistic model, the numerous factors that can continue to be used for risk prioritization and establishing inspection effectiveness are included. If an equipment item requires higher level analysis, the same model can be applied to a Level 2 or 3 assessment having a consistent basis. Inspection results can also be used to adjust the metallurgical factors that lead to a given void spacing (damage density), rather than relying on typical lower bound assumptions as done in screening, thereby decreasing the uncertainties in modeling.

## REVISITING YOUR HTHA ASSESSMENT PROGRAM

Given the large advances in NDE technology and the advances in modeling described herein, the operator may want to revisit their management plan for HTHA. Below is a checklist/questions you may want to ponder as you embark on that HTHA re-assessment.

- Have I considered all of my operating history, including abnormal and upset conditions? Have I filtered out downtimes or bad data?
- How confident am I about the early years of this asset's history before there were digital control systems (DCS)?
- How effective have past HTHA inspections been (scope and method), given the new API 941 Appendix E methods/advice? How do I give credit in reducing uncertainties in the remnant life prediction for future inspection results?
- Have I considered the stress state and materials properties given metallurgical factors?
- If my operating conditions have changed, how can I account for varying conditions and predict a remaining life?
- Can I calculate where my asset will be on its remaining life curve in future years, like a decade hence?
- Can I pinpoint where NDE inspections should focus and when I should replace/upgrade equipment?

## CONCLUSION

The Nelson Curve has generally served industry well over the last 60 years but has shown gaps where abnormal service has occurred. While Becht has done many screening evaluations using the Pono HTHA Evaluation Method to risk prioritize equipment, we used the Nelson curves as curve fits and adjusted them based on empirical knowledge. Early on, the Pono Method did not allow for direct use of pertinent information in more detailed analysis and/or combining different operating scenarios. With the generation of mechanistic time-based Nelson curves published here, we now have the ability to get more precise with predicting failure times and locations for damage and inspection, given the operating conditions. We believe the model presented in this article bridges that gap between practical industry experience and the underlying mechanistic behavior. We hope with this

greater precision, owner-operators can make better risk-informed decisions in managing their HTHA susceptible equipment as it ages. ■

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