Managing the risk of damage due to high temperature hydrogen attack (HTHA) has been a major problem for the synthesis gas industries. The reasons for this are largely twofold: firstly, the likelihood of HTHA occurring has proven difficult to predict and, secondly, the detection of HTHA by inspection is problematic. Given the potential for extreme consequences in the event of a catastrophic release of hydrogen (as seen in the Tesoro Anacortes incident in 2010), the need for a multifaceted approach based upon an integrated risk management plan is imperative. The risk is illustrated in Figure 1, which shows the hydrotreater exchanger that failed at Tesoro and resulted in seven fatalities. This photograph is much reproduced but remains an important reminder of the potential for catastrophe caused by unchecked HTHA damage.

This article describes recent experiences relating to damage found in equipment that may have been considered safe using traditional approaches to managing risk, as well as the inspection techniques required to detect that damage.

HTHA
The process of HTHA requires the dissolution of atomic hydrogen. This is normal as all ferritic steels operating in hydrogen at an elevated temperature and pressure will dissolve hydrogen. The higher the temperature and pressure, the greater the amount of dissolved hydrogen. Another manifestation of this phenomenon is the frequent need to ‘bake-out’ or heat treat steels in order to remove the dissolved hydrogen before attempting the welding of steels. The dissolved hydrogen is reactive; it will react with any free
carbon or internal carbides, both of which have significant influence on material strength.

This carbon and/or carbide reaction generates methane gas. The more stable the carbides in the steel, the less likely the reaction is to occur. Consequently, more alloyed grades are more resistant to HTHA. Methane is not soluble, and forms in small pockets around internal inclusions. The localised pressures here can be extremely high, and localised high stress levels are generated leading to the formation of internal fissures and micro-cracks. Near-surface pockets of methane can lead to blistering. The formation of micro-fissures and the loss of carbon results in serious reductions in strength, ductility and toughness. The reduction of these material properties will ultimately result in the component being unable to withstand the normal service loads, and catastrophic failure will occur (Figure 1). Figure 2 shows an example of the internal micro-fissuring caused by HTHA, which must be either prevented or detected by advanced inspection.

The Nelson Curves

For many years, significant confidence has been placed in the Nelson Curves, as described in API 941, to predict the likelihood of HTHA. These curves are based on reported performance and have been subject to a number of significant changes as new experiences come to light. Figure 3 shows the Nelson Curve from API 941. This set of curves represents the core information in the API standard. In the 1990s, there was a growing number of cases of HTHA damage occurring in carbon-1/2molybdenum steels. As a result, the carbon-1/2molybdenum curve was removed from the API 941 guideline, thereby placing a large volume of carbon-1/2molybdenum equipment in limbo alongside the recommendation that the material should be treated as carbon steel as far as its resistance to HTHA was concerned. Due to this API 941 addendum, a large number of affected equipment already in-service and designed to the original carbon-1/2molybdenum curve was operating above the carbon steel curve.

An attempt was made to rationalise the experience with carbon-1/2molybdenum steel by providing different risk factors for annealed and normalised material. The implication is that the metallurgical condition of the material, in this case the form and stability of the carbides, was significant. There is, however, no reason to believe that such an effect is unique to carbon-1/2molybdenum steel or indeed parent metal as opposed to weld and HAZ material. An attempt to quantify risk factors using a parameter Pv dependent on pressure, temperature and operating pressure was included in the 2008 version of API 581, but this was removed from the 2016 version.

The second major change occurred in the wake of the Tesoro incident and the subsequent Chemical Safety Board Report. The investigation concluded that failure of the exchanger occurred due to HTHA in a carbon steel pressure shell that was operating below the Nelson Curve. Significantly, the exchanger had not been post weld heat treated, and all the observable damage was present in the heat affected zone. API 941 contains comprehensive information concerning the influence of stress on the risk of HTHA. The 2016 edition contains the first attempt to quantify this by introducing a new curve for carbon steel that has not been post weld heat treated.

As in the case of metallurgical condition, there is no reason to believe that the effect of stress is unique to one particular grade of steel. However, it is very likely that more highly alloyed grades will be post weld heat treated. As API 941 details, the risk of HTHA in steels that operate within the ASME allowable stress limits, and below the Nelson Curves, is negligible. The influence of stress does need to be taken into account when severe stresses (such as weld residual stress, thermal stress or high piping loads) exist. Being aware of the existence of such stresses is an essential part of any risk management plan.

Despite these limitations, API 941 and the Nelson Curves remains the principal guide to managing the risk of HTHA. It is an experience-based document and continuous modification in the light of new information is to be expected. By themselves, the Nelson Curves do not guarantee freedom from HTHA.

Risk assessment

As noted above, the API 581 approach to establishing risk levels using a single quantifiable parameter Pv has been removed from the recommended practice. The 2016 version has adopted a very conservative approach, particularly for carbon and carbon-1/2molybdenum steels. For these steels, the current version API 581 assigns high susceptibility for any component operating above 177˚C (350˚F) with a hydrogen partial pressure exceeding 0.345 MPa (50 psia). This is very conservative relative
to the API 941 Nelson Curves for both post weld heat treated and non-post weld heat treated carbon steels. It is acknowledged, however, that this is an interim measure while a more quantitative method is under development.

For low alloy steels, the calculation of risk factor has also been simplified through the acknowledgement that the Nelson Curves do not represent an absolute measure of risk, but that assigning a risk level based upon the margin by which any component operates below the Nelson Curve is advisable (Figure 4). This high level of conservatism on the one hand, and scepticism around the reliability of the Nelson Curves on the other, has led some owners to develop their own methodologies. An example approach is summarised below.

**Step 1: identifying susceptible equipment**
All equipment in hydrogen service is identified and categorised as:

- High susceptibility: operating on or above the Nelson Curve.
- Low susceptibility: operating below but within a 50˚F and 50 psi below the curve.
- No susceptibility: operating more than 50˚F and 50 psi below the curve.

**Step 2: undertake risk assessment**
For all equipment that is identified as being susceptible to HTHA, a risk assessment is performed. Using standard risk methodologies, a risk matrix can be generated. The factors to be taken into account for HTHA include:

- Temperature.
- Hydrogen partial pressure.
- Material of construction.
- Exposure time.
- Stress.
- Cladding.
- Previous failures.

**Step 3: develop a risk management plan**
A primary objective would be to reduce the risk for those assets in which the risk is assessed to lie within the ‘high risk’ (red) area of a risk assessment matrix. This may be achieved in the short-term to allow operation to the next scheduled outage by reducing operating conditions, usually by adjusting temperature. Long-term solutions involve:

- Developing robust inspection test plans (ITP). This may include destructive testing.
- Enact inspection to be conducted at scheduled outages. If HTHA is found, the consideration of equipment replacement with upgraded metallurgy is advisable.

**Step 4: integrate with asset integrity management plan**
It is critical for ongoing risk management that knowledge and operational limits be understood and acted upon within the wider organisation. Key issues that must be addressed include:

- Knowledge, training and knowledge management: it is essential that the significance and risk of HTHA (and indeed all potential damage mechanisms) are understood throughout the organisation.
- Establishment of integrity operating windows (IOWs): the risk of HTHA is strongly influenced by operating conditions. Establishing and implementing IOWs is required to ensure continuing operation. This should include reporting protocols so that the impact of any excursion can be assessed.
- Plant standard operating procedures (SOPs): the impact of HTHA should acknowledge the significance and risk of HTHA and the control measures that are in place to manage that risk.

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**Figure 3. Operating limits for steels in hydrogen service to avoid HTHA.**

- Inspection history.
Management of change (MOC): robust MOC procedures are required to ensure that any changes to operating conditions do not impact negatively on the reliability of the plant.

Inspection
The risk management plan for each piece of equipment that is deemed susceptible to HTHA inevitably calls on inspection to determine the presence and extent of HTHA. The ultimate control of HTHA is to replace at-risk equipment. This is usually a costly solution and justification would normally require evidence that HTHA damage had indeed occurred. API 941 contains commentary on the various candidate inspection techniques and concludes that no single inspection technique is ideally suited to detection of HTHA damage, particularly in its embryonic stage when micro-fissuring is just beginning to form.

Ultrasonic inspection (UT) has been found to have the best chance of detecting HTHA. Four generic types have been used, as listed below:

- Backscatter techniques.
- Velocity methods.
- Attenuation.
- Spectral analysis.

These are illustrated schematically in Figure 5. Backscatter UT involves irradiating the test material with moderately high frequency ultrasound and measuring the backscatter noise that is reflected from HTHA. This can be used to detect HTHA and also to provide an estimate of the concentration and through thickness extent of damage.

Velocity methods make use of the fact that the altered microstructure from HTHA produces material with different shear wave ultrasound velocity than the unaffected material, whereas compression wave ultrasound velocity is relatively unaffected.

The backwall reflection is essentially a wall thickness test: the extent to which the signal is attenuated by the presence of HTHA can be used to characterise the extent of HTHA and differentiate HTHA from other forms of damage.

An extension of this technique is spectral analysis in which the dependence of attenuation on the frequency of the ultrasonic signal is analysed. The higher frequency spectrum from the reflected backwall of a broad band ultrasonic signal is more extensively attenuated. Such analysis can help differentiate between HTHA and other apparent damage, such as embedded defects. The success of this approach is dependent on the sampling technique, which can be impaired by the following factors:

- Non-parallel material geometry.
- Thin wall tube.
- Austenitic clad material.
- Localised damage at weldments.
- Inherently attenuative material.

None of these techniques are ideal, and an inspection methodology has been developed that uses all four. This is the advanced ultrasonic backscatter technique (AUBT). In this methodology, backscatter methods are used as screening tool to locate damaged areas, and based upon the backscatter pattern observed, one or more of the other UT techniques are employed to qualify the presence of HTHA damage. A rigid approach to the characterisation of the damage from the ultrasonic methods, in all situations, will not provide a successful result. Success depends on the operator’s ability to assess, select appropriate methodologies and analyse the data.

The AUBT technique and its variants have been used extensively in the integrity management and inspection programmes at Incitec Pivot Plants (IPL). The results are summarised in Table 1.

Historical analysis of HTHA inspection at IPL has indicated a strong dependence on the knowledge and experience of the operator performing the inspection. AUBT inspections that have been contracted without first qualifying the inspection

![Table 1. Results of the inspection programme](image)

<table>
<thead>
<tr>
<th>Item</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment items assessed susceptible to HTHA</td>
<td>75</td>
</tr>
<tr>
<td>Equipment items inspected for HTHA</td>
<td>36</td>
</tr>
<tr>
<td>Equipment items confirmed to have HTHA</td>
<td>22 (61% of inspected items)</td>
</tr>
<tr>
<td>HTHA identified by AUBT</td>
<td>1</td>
</tr>
<tr>
<td>HTHA identified by AUBT with qualified operator</td>
<td>18</td>
</tr>
<tr>
<td>HTHA confirmed by metallurgical sample</td>
<td>2</td>
</tr>
</tbody>
</table>

![Figure 4. An example risk assessment for low alloy steels in an HTHA environment (API 581).](image)

![Figure 5. Schematic illustrations of UT inspection techniques for HTHA.](image)
personnel have been largely unsuccessful. However, the inspections performed by inspectors in which the owner had confidence have proven very successful. In this context, a ‘qualified’ inspector is one that has verified that the methods, and procedures employed during the inspection have a very high chance of detecting HTHA, if present. It does not mean that the inspector has a certificate confirming attendance to an HTHA training course.

Given the absence of any single or reliable UT technique to detect HTHA, the findings at IPL have been that the experience and the knowledge of the inspector is paramount to the success of the inspection programme. The importance of a robust asset integrity management programme was noted previously, and a number of the activities that go to make such a programme were highlighted. The results of the HTHA inspection programme at IPL firmly emphasised the importance of other factors in such a programme, including:

- Approval procedures for service providers.
- Critical review and statistical analysis of inspection results.

In the case of HTHA, it is strongly recommended that plant owners develop an inspection programme for HTHA in partnership with their selected inspection provider, and that these relationships be maintained in the long-term, in order to fully optimise plant assets.

**Conclusion**

The experience of managing HTHA at IPL has highlighted the importance of a robust asset integrity management programme. HTHA cannot be effectively managed in isolation by simple inspection, and a number of factors must be carefully considered in order to maximise the likelihood of detecting and controlling the risk that this damage mechanism presents. Operating such a programme is a continuous activity. It is important to consider the link between risk level and decision making, particularly as it relates to capital expenditure. It is also critical to ensure that all staff appreciate the risk. In order to guarantee this knowledge is gained, it is important that ongoing IOWs, SOPs and training programmes are developed to reflect the risk associated with HTHA.

Inspection for HTHA is an essential part of the asset integrity management programme and it has been found that such inspection is a particularly difficult task requiring significant expertise. Successful detection and quantification of HTHA requires the ability to select the most appropriate technique for any given inspection challenge and optimise that technique. The skill and experience of the inspection personnel is paramount to the success of the inspection, and must be demonstrable to standards embedded in company procedures and practices.

**References**