GUIDELINE ON REMEDIAL ACTIONS FOR HYCO PLANT COMPONENTS SUBJECT TO HIGH TEMPERATURE HYDROGEN ATTACK

FIRST EDITION

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PREFACE

As part of a program of harmonisation of industry standards, the European Industrial Gases Association (EIGA) has published, EIGA Doc 243, *Guideline on Remedial Actions for HYCO Plant Components Subject to High Temperature Hydrogen Attack,* jointly produced by members of the International Harmonisation Council and published by the Compressed Gas Association (CGA) as *CGA H-16 Guideline on Remedial Actions for HYCO Plant Components Subject to High Temperature Hydrogen Attack.*

This publication is intended as an international harmonised standard for the worldwide use and application of all members of the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), and Japan Industrial and Medical Gases Association (JIMGA). Each association's technical content is identical, except for regional regulatory requirements and minor changes in formatting and spelling.

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1 Introduction

Industrial gas companies operate and maintain hydrogen production facilities worldwide ranging in scale from small (< 1MM SCF per day) to the world's largest facilities (> 150MM SCF per day). These plants, and the related HYCO facilities that produce carbon monoxide and syngas products, generally involve the handling of flammable gases at high temperatures typically up to 925 °C (1700 °F) and moderate to high pressures. These processing conditions can present inherent hazards that should be recognized and properly managed to ensure the mechanical integrity and safe operation of the facilities. One such hazard is a phenomenon known as High Temperature Hydrogen Attack (HTHA).

HTHA is a mechanism that can significantly weaken and damage a variety of steel materials that are used in the construction of hydrogen plants, including carbon steel and various low alloy steels. The hydrogen molecules contained in many hydrogen plant process streams can dissociate to atomic hydrogen and diffuse into the steel and react with carbon to form methane that creates fissures that will grow and weaken the steel structure. The initiation of this reaction and the rate of reaction is primarily dependent on steel type, hydrogen partial pressure, and temperature. The cumulative amount of exposure time to these conditions will dictate the degree of degradation of the material strength. For this reason, equipment operated in the HTHA concern zone becomes more susceptible to damage over time and requires regular examination.

The issue of HTHA is known and documented within the oil and gas Industry, most notably in the API RP 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants* [1].[1] However, HTHA related failures have not been eliminated in part because API RP 941 is empirically based [1]. A significant incident that occurred in 2010 was the HTHA-induced catastrophic failure of a heat exchanger at a Tesoro refinery in Anacortes, Washington, United States. This tragic event led to an investigation by the United States Chemical Safety and Hazard Investigation Board (CSB) and subsequently a revision of API RP 941 [1]. That revision included a change to the HTHA limits, known as the Nelson Curves, which are used to determine the maximum operating temperature and pressure for carbon and low alloy steels in hydrogen-rich service. For more details, see CSB Report 2010-08-I-WA, May 2014, *Tesoro Refinery Fatal Explosion and Fire* and API RP 941 [2, 1].

Based on the revisions made to API RP 941, EIGA has identified this API document as the Recognized and Generally Accepted Good Engineering Practice for assessing HTHA risk [1].

Given the API RP 941 revised Nelson Curves, carbon steel might no longer be considered an appropriate material in certain services in HYCO plants (e.g., the mixing tee where steam and feed are mixed in a steam methane reformer [SMR] process gas boiler outlet line), although the damage mechanism can take a long time to develop to failure [1]. Operational HYCO plants (including hydrogen/CO/syngas plants) need to be aware that the design criteria for carbon steel and other low alloy steels in hydrogen-rich service have changed. A review of existing components that are vulnerable to HTHA (per API RP 941) in hydrogen-containing services is likely required [1].

This publication will provide guidance, heuristics, and some examples of methodologies for the review of existing HYCO plant assets to determine their potential for HTHA-initiated cumulative damage. It will also provide guidelines for risk categorization, inspection strategies, and recommendations on risk mitigation.

2 Scope

This publication will identify actions for the owners and operators of HYCO plants (including carbon monoxide and syngas plants) in response to the updated guidance on the HTHA mechanism documented in API RP 941 [1]. This publication can apply to all scales of hydrogen production and consumption facilities that utilize the relevant materials of construction.

[1] References are shown by bracketed numbers and are listed in order of appearance in the reference section.

Risk of the HTHA mechanism will be determined for the components that are exposed to hydrogen-containing gas at a temperature above 205 °C (400 °F) (with some margin below 205 °C (400 °F) to allow for uncertainties). Examples of services in a HYCO plant that would typically require assessment are provided in Section 8.

It should be noted that there are other industries that operate hydrogen or syngas producing plants for purposes other than hydrogen production. For example, the ammonia and methanol industry operate syngas production facilities and should find relevant guidance from this publication.

This publication is not intended to address the details of design or construction of new facilities relative to HTHA. Please note that in this publication, the term “low alloy steels” refers to chromium-molybdenum (CrMo) steels.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 Chromium-molybdenum

Grades of steel with chromium and molybdenum added to increase strength and hardness compared to carbon steel.

NOTE—They have lower levels of chromium compared to stainless steel and thus lower corrosion resistance.

3.2.2 Cladding/weld overlays

Use of a corrosion-resistant alloy to protect a lower grade metal which is the primary pressure boundary. The cladding can be bonded to the base layer through one of several methods (e.g., weld overlay, explosive bonding, etc.).

3.2.3 Decarburization

Loss of carbon in metal that results in loss of hardness and strength. In the case of HTHA, the carbon is lost via reaction with hydrogen to methane.

3.2.4 Hydrogen partial pressures

Pressure attributed to only the hydrogen portion of a process fluid.

NOTE—See 7.2.2 for more information on calculating hydrogen partial pressure.

3.2.5 Inspection test plans

Program of inspection and monitoring to prevent loss of containment.

NOTE—Inspection test plans are also sometimes referred to as mechanical integrity inspection plans.

3.2.6 Low alloy steels

Family of steels containing up to 9% chromium and/or other alloying additions for high temperature strength and creep resistance.

NOTE—Chromium-molybdenum steels are one category of low alloy steels.

3.2.7 Management of change

Formal monitoring program in which qualified representatives of appropriate disciplines review proposed or actual changes that can affect a validated status.

NOTE—Management of change is often referred to as change control.

3.2.8 Nelson Curves

Chart with curves of HTHA operating limits for various steel grades for hydrogen partial pressure and operating temperature.

3.2.9 Nondestructive examination (NDE) techniques

Methods of testing material without damage to the material. Examples include ultrasonic, magnetic particle, radiographic, and liquid penetrant.

NOTE—NDE is also sometimes referred to as nondestructive testing (NDT).

3.2.10 Post weld heat treatment

Process where material that has been welded is subsequently heated and held at a prescribed temperature for a period of time in order to reduce residual stress and return other properties to acceptable levels.

NOTE—This is the primary tool from API RP 941 for assessing HTHA risk [1].

3.2.11 Refractory lined (internally insulated) equipment

Equipment that utilizes an internal refractory layer so the metal pressure boundary is at a lower temperature than the process fluid contained to reduce stress. Typically, the lower stress allows for a lower grade of metal or thinner wall in the pressure boundary.

4 General safety

HYCO plants operate at high temperature and pressure, and both the feed and product streams contain flammable and/or toxic components. The intermediate product (syngas) and final product streams of HYCO plants typically contain a high fraction of hydrogen and the feed stream(s) can also contain a significant fraction of hydrogen (either present in the feed or added via recycle), depending on the type of feed.

Depending on the hydrogen partial pressure and temperature of a given stream, the associated piping or equipment could be subject to HTHA. HTHA manifests as localized, microscopic cracks, such that identifying its presence can be difficult. HTHA can eventually cause piping or equipment failure, which could result in the release of a flammable and/or toxic fluid at high temperature and/or pressure. Such failures, some resulting in fatalities, have occurred in the broader hydrocarbon processing industry.

Because the rate of HTHA is influenced by operating conditions, it is important to identify the conditions that will be present in all operating modes. All known operating modes shall be considered when evaluating the risk of HTHA and when selecting the materials for new plant designs and retrofits of existing facilities. Existing plants should assess actual process conditions in all operating modes and factor any differences relative to design into the HTHA risk assessment.

5 Mechanism

HTHA is a damage mechanism that occurs at elevated temperatures and pressures when atomic hydrogen diffuses into the metals and reacts with carbon and certain metal carbides. The reaction can decarburize the metal surface, and/or form methane gas voids and fissures inside the metals if diffusion of carbon to the surface is limited.

The Nelson Curves in API RP 941, which are based on industrial successes and failures as well as laboratory experiments (i.e., empirically based), define temperature and hydrogen partial pressure limits for different materials, above which HTHA is highly probable [1].

At relatively high temperature and low hydrogen partial pressures, the damage is manifested by surface decarburization, whereas at relatively low temperature and higher hydrogen partial pressure, internal voids and microfissures are favored. The more likely manifestation, dependent on conditions, is indicated on the Nelson Curves.

The methane gas formed internally accumulates at grain boundaries, inclusions, and precipitate interfaces. As the internal methane gas pressure and volume increases, the small voids and fissures can grow and connect, forming larger cracks and eventually leading to a through wall failure. Microscopically, decarburized microstructure usually presents in the vicinity of the internal voids and fissures. Surface decarburization is of less concern to pressure boundaries, but it can be a sign of internal damage.

HTHA damage is irreversible and cumulative over the time. The time preceding any detectable damage by non-destructive technology and metallographic analysis is called the incubation period. Mechanical properties are not affected during the incubation period. Deterioration of mechanical properties is accompanied by the growth of the internal fissures. API RP 941 provides curves of the incubation time for non-welded or welded with post weld heat treatment (PWHT) carbon steel [1].

Susceptible materials include both as-welded and PWHT carbon steels, as well as certain low alloy steels. Materials with elements that can form more stable metal carbides (such as chromium, molybdenum, tungsten, vanadium, titanium, and niobium) reduce the tendency of HTHA. Therefore, modified carbon steels and low alloy steels with added carbide stabilizing elements can be suitable for resisting HTHA. PWHT, which stabilizes carbides and reduces residual stresses, improves resistance to HTHA. Applied and residual stresses can also affect the rate of and susceptibility to HTHA.

6 API RP 941 overview

API RP 941 is the recognized and generally accepted good engineering practice for selecting materials respective to their resistance to HTHA [1]. This document utilizes extensive operating history (both successful operations and failures) for the various materials and operating conditions.

6.1 The Nelson Curves

The primary tool within API RP 941 is known as the Nelson Curves, which are experience-based curves for various material classes that are at risk for HTHA [1]. The Nelson Curve axes are process temperature and hydrogen partial pressure. The intent is that materials in question are operated below the relevant curve.

Importantly, the process conditions are to be coincidental, i.e., the operating temperature should be compared to the hydrogen partial pressure occurring at the same time, and not the maximum possible hydrogen partial pressure. This factor is important for equipment that can have multiple operating cases.

Stress levels in piping and equipment impact susceptibility to HTHA. As API RP 941 states, the risk of HTHA in steels that operate within the ASME allowable stress limits, and below the Nelson Curves (with adequate margin), is negligible [1]. The influence of stress does need to be taken into account when elevated primary stresses (e.g., nozzle loads), secondary stresses (e.g., thermal stress) and local stresses (e.g., weld residual stress) exist. PWHT provides benefit by reducing local stress levels and stabilizing carbides in carbon steel and low alloy steels. Being aware of the existence of such stresses is an essential part of any risk management plan. Consult API RP 941 for more details on stress and the benefits associated with PWHT [1].

The impact of cladding/weld overlays on material selection is also addressed in API RP 941 [1]. Importantly, it should be noted that while the cladding material might not be subject to HTHA (e.g., stainless steel), hydrogen can still penetrate to the underlying base material and HTHA can occur in the base metal.

In the 1990s, a growing number of cases of HTHA damage occurring in Carbon-1/2 Molybdenum (C-0.5Mo) steels resulted in the removal of the Carbon-1/2 Molybdenum curve in the 4th edition of API RP 941 [1]. It was recommended that this material should be treated as carbon steel with PWHT as far as its resistance to HTHA was concerned. Because of this API RP 941 addendum, some affected equipment already in-service and designed to the original Carbon-1/2 Molybdenum curve now operate above the updated carbon steel with PWHT curve [1]. Annex A in API RP 941 addresses Carbon-1/2 Molybdenum materials [1].

The 8th edition of API RP 941 separated the carbon steel curve into separate curves for “welded without PWHT” and “PWHT or non-welded” [1]. This change was made based on experiences indicating a significant difference in HTHA resistance for similar materials with and without PWHT.

API RP 941 remains the principal guide to managing the risk of HTHA [1]. API RP 941 is an experience-based document and periodic updates in the light of new information are to be expected [1]. HTHA risk assessments should be reevaluated in response to such periodic updates of industry standards.

6.2 Safety margins

API RP 941 notes that the data for the Nelson Curves are based on actual operating conditions and empirical experience [1]. Thus, safety margins should be added below the curves when evaluating equipment and piping to account for the many factors including transient conditions, measurement inaccuracies, and lack of direct condition measurement.

API RP 571, *Recommended Practice on Damage Mechanisms Affecting Fixed Equipment in Refining Industry*, which includes a section on HTHA, provides typical design margins applied to temperature and hydrogen partial pressure when using the API RP 941 curves [3, 1].

7 Assessing and addressing high temperature hydrogen attack risk at existing plants

7.1 Screening for high temperature hydrogen attack susceptibility

Susceptibility to HTHA depends on several factors, but the three most important are:

- material of construction;
- exposure temperature; and
- partial pressure of hydrogen in the process.

For a given material, a lower bound screening (temperature and hydrogen partial pressure) criterion should be established. Any equipment that operates below these criteria can be excluded from the HTHA risk assessment.

The temperature for exclusion from HTHA assessment is set below the applicable Nelson curve. A typical temperature margin is 28° C (50° F), but the margin will depend on the quality of the information available. A margin for hydrogen partial pressure shall also be considered (e.g., use design pressure rather than operating pressure in the partial pressure calculation). This is meant to be a conservative assessment.

API RP 581, *Risk-Based Inspection Methodology* provides a methodology for assessing the risk of HTHA in operating plants, assigning a risk level based on the operating conditions (temperature and partial pressure) relative to the applicable API RP 941 Nelson Curve [4, 1].

7.2 Information and data collection

Typically, HTHA risk assessments focus on carbon steels and low alloy steels. Low alloy steels require higher temperatures before HTHA occurs and therefore are less likely to experience HTHA in normal refinery environments. Still, one needs to assess all operating conditions against the respective alloy's Nelson Curve before determining the likelihood for HTHA. To do this properly, the next step is to collect information and data on each piece of equipment and piping circuit that falls within the screening criteria identified in 7.1.

Information and data collected/verified should, at a minimum, include the following:

- installation date or, if the equipment has been replaced, the replacement date;
- detailed equipment drawings;
- materials of construction, including all components;
- confirmation of PWHT, where applicable;
- identification of any cladding, liner, or overlay present;
- thickness of any existing cladding, liner, or overlay;
- presence of refractory lining (cold wall design);
- inspection history;
- documentation on repairs and procedures employed;
- design data (pressure and temperatures); and
- operational data, including process temperatures, hydrogen partial pressures, and external metal surface temperatures.

Operational data are extremely critical and can be the most challenging data to compile with an acceptable confidence in accuracy. If operational data are not properly collected and verified, it can result in incorrectly defining HTHA susceptibility and/or a flawed HTHA risk assessment.

7.2.1 Determination of process temperatures

Existing temperature data should be investigated to the earliest date of the operating history. This data analysis can be different from one point to another, depending on how close the temperatures are to the point where HTHA risk becomes an issue. For instance, if by drawing a horizontal temperature line on a time dependent plot (assuming a worst-case temperature profile) no HTHA risk is realized, that can be the end of the temperature data review for the components associated with that temperature point. If the temperatures occasionally exceed the user defined HTHA limit, or vary from start to end of run, a more detailed analysis might be needed. Process temperatures may also be estimated through calculations or process simulations.

Temperature data might only be available for a small portion of the plant. If no process stream temperature data are available, it is possible to measure external surface temperatures with IR devices or other means. While this does not provide historical information, it can support correlations to estimate temperature where no historical data is available. If the conditions are estimated to be inside the screening criteria, additional testing may be completed to confirm benchmark conditions.

7.2.2 Determination of hydrogen partial pressure

To determine the hydrogen partial pressure, multiply the mole fraction of hydrogen in the process stream by the absolute pressure of the stream. A good place to start is with the unit's heat and material balance, but the values should be compared to actual operating data. If there are significant differences between the original heat and material balance and the actual conditions, one should check if any management of change (MOC) documents evaluated the change in conditions.

If the stream contains liquid hydrocarbon and if hydrogen is dissolved in the liquid hydrocarbon, the hydrogen partial pressure is calculated differently. One method, cited in API RP 941, involves using the vapor pressure of the gas with which the liquid stream is in equilibrium [1]. This is an important point since if there is a liquid stream, one might assume the amount of hydrogen present is very low, which could lead to underestimating the partial pressure of the gas.

7.3 Assessing high temperature hydrogen attack risk

With the information assembled, the next steps can be taken.

7.3.1 Step 1—Identify equipment and piping in susceptible service (i.e., process conditions and metallurgy are inside the screening criteria)

Select appropriate safety margins relative to each applicable Nelson Curve (see 7.1). Identify all equipment that operate or have operated within this range. See API RP 581 for more details [4].

7.3.2 Step 2—Assess risk of HTHA

For all equipment that falls within the at-risk operating region, evaluate the level of HTHA risk based on the following factors and develop a risk matrix using standard risk methodologies. The factors to be taken into account for HTHA include:

- Temperature;
- Cladding/weld overlays—Austenitic stainless steel has higher hydrogen solubility and lower hydrogen diffusion coefficient than the non-austenitic base metals, which reduces the rate of hydrogen diffusion into the underlying steel. In the presence of cladding or overlaid steel, it is important to first verify that the inspection history validates the integrity of the overlay (no cracks, tears, or bulges). The effective hydrogen partial pressure at the interface between the barrier and base metal also needs to be calculated to establish how much protection from HTHA the barrier is providing. The methodology on how to do this (including the formula for calculation of effective hydrogen partial pressure) is provided in the API RP 941, Annex D [1]. Note that loose liners or ferritic stainless steels (such as type 405 or 410) are not considered adequate for reducing the likelihood of HTHA;
- Hydrogen partial pressure;
- Prior failures;
- Material of construction;
- Inspection history—This history can give the user better information and should be considered during the risk assessment. Questions to answer are:
    - Has the component ever been inspected for HTHA
    - What techniques were used and what was the outcome
    - How much of the component was inspected;
- Exposure time (age)—HTHA has an incubation time based on process conditions. The longer a particular component has been exposed to conditions above the HTHA limits established, the more likely the effects of HTHA will be experienced;

- Heat treatment—If there are components that have been subject to PWHT, their risk for HTHA is different from other components; and this should be taken into consideration during the risk assessment; and
- Stress.

7.3.3 Step 3—Develop risk management plan

Based on level of risk, develop an equipment targeted risk management plan for those assets determined to be susceptible to HTHA. This may be achieved in the short term by adjusting operating conditions, such as by reducing temperature and/or partial pressure of hydrogen, to allow operation until an outage. Long term solutions could involve:

- Proactive replacement of equipment or piping with upgraded metallurgy with consideration to the Nelson Curves to minimize or eliminate the risk of HTHA; or
- Inspection and monitoring, which would include:
  - Development of inspection test plans (ITP). This may include destructive testing. Consult API 941, Appendix E for detailed discussion on ITP [1];
  - Performing inspection at the next outage; and
  - If HTHA is found, performing fitness for service assessment to consider equipment repair or replacement with upgraded metallurgy.

7.3.4 Step 4—Update site mechanical integrity program.

Integrate the HTHA risk management plan with the overall site mechanical integrity program. It is critical for the ongoing management of risk that knowledge and operational limits be understood and acted upon with the wider organization. Key issues that should be addressed include:

- Identify the significance and risk of HTHA in the overall site mechanical integrity program;
- Establish and implement safe operating parameters (i.e., integrity operating window [IOW]) with deviations alarmed in the control system. Consult API RP-584, *Integrity Operating Windows* [5]. This should include reporting protocols so that the impact of any excursion can be assessed and acted on appropriately;
- Update plant standard operating procedures (SOP). The impact of HTHA should be acknowledged and control measures identified to manage that risk; and
- Follow the site MOC process, including updating HTHA assessment.

8 Likely areas of concern/identification of assets

Based on typical HYCO plant designs and conditions, certain areas of the plant are more likely to operate at conditions where the materials are susceptible to HTHA.

8.1 Feed purification systems

The front-end purification systems used for sulfur removal from the hydrocarbon feed in HYCO plants are typically made from either carbon steel or low alloy materials. In case of carbon steel construction, HTHA risk can be reached depending on the hydrogen partial pressure, as the typical operating temperatures are above the HTHA limits for this material. If the feed to the plant does not contain hydrogen, typically a small amount (1% to 2% of the feed) is added to help with sulfur removal. Due to the low level of hydrogen, the partial pressure will be below the HTHA limit of 345 kPa, abs (50 psia). [2] However, review of operating conditions should be conducted, and arrangements should be made to avoid higher hydrogen concentrations in cases such as operating the plant at rates much lower than

[2] kPa shall indicate gauge pressure unless otherwise noted as (kPa, abs) for absolute pressure or (kPa, differential) for differential pressure. All kPa values are rounded off per CGA P-11, *Guideline for Metric Practice in the Compressed Gas Industry* [6].

design. Consider adding an alarm and recording the time of exposure if instrumentation failure could result in exceeding 345 kPa, abs (50 psia) hydrogen partial pressure at turndown.

Offgas feeds typically include significant levels of hydrogen such that the resulting partial pressure will likely exceed the HTHA limits for carbon steel at feed purification temperatures. Plants which are initially designed for such feeds will typically use low alloy materials. However, in cases of a change in feed stock to include these streams, owners should be aware that the purification system metallurgy might not be sufficient if constructed from carbon steel. Additionally, some means of monitoring gas composition should be considered for offgas feeds containing hydrogen.

8.2 Refractory lined equipment

Many HYCO facilities use pressurized refractory lined equipment operating at high temperatures. This lining allows the pressure boundary to be at much lower temperatures compared to the process fluid so that the shell can be designed with higher allowable stresses and lower metallurgical grades. Examples of these equipment include prereformers, reformer outlet transfer lines, process waste heat boiler heads, and autothermal reformers.

Refractory lined equipment is frequently made from materials at risk for HTHA and contains fluids above the HTHA partial pressure limits . Therefore, the metal shell temperature shall be reviewed and monitored to avoid exceeding the HTHA limit . While most equipment is designed have an expected and normal operating temperature below the HTHA limit , if the refractory degrades during operation, the shell temperature will increase and can reach the HTHA limit. In the case of carbon steel shells, the equipment designer might not consider HTHA and could establish a design temperature for the shell that is above the HTHA limit. In these cases, the plant HTHA review should identify the HTHA limit so that operations personnel will know the correct point at which to take actions.

All pressurized refractory lined equipment should be monitored for increasing shell temperature due to refractory degradation.

For more information on the safe operation of refractory-lined equipment, see EIGA Doc 202, *Mechanical Integrity of Syngas Outlet Systems* [7].

8.3 Shift reactors and syngas cooling train

In typical HYCO plants, equipment downstream of the primary syngas generation will be at conditions above the minimum HTHA concern temperatures before being cooled to approximately ambient temperatures. This equipment may include shift reactors (in hydrogen plants) and various exchangers and condensate knockouts. A typical metallurgical selection will be low alloy in the initial equipment, switching to stainless steel at the point where condensation can form.

Low alloy equipment will usually be at temperatures below their HTHA limits. The primary concern will be with carbon steel equipment. In some plants, carbon steel equipment is used as an intermediate step between low alloy steel and stainless steel. Due to changes in the Nelson Curves, this piping and equipment might now be considered susceptible to HTHA. Additionally, some older equipment might utilize low alloy material, which should be evaluated based upon the guidance in API RP 941 [1].

8.4 Dryers

Equipment with multiple operating conditions require additional HTHA review. An example of this condition is molecular sieve dryers, which utilize heating for regeneration. Generally, the drying phase will be done well below the HTHA temperature limit. The regeneration stage should be reviewed thoroughly but will often be below the HTHA hydrogen partial pressure limit.

Ensure all operating conditions, such as the transition from regeneration to on-stream operation, are also considered. When a dryer has completed the regeneration step and is ready to return to drying, the review shall consider if the bed pressure is increased before temperature has been fully cooled.

9 Inspection and monitoring methodology

Piping and equipment that has been determined to be susceptible to HTHA can require inspection to determine if HTHA is present and, if so, to what extent. Alternatively, equipment can be replaced proactively, but the timing of the equipment replacement needs to be evaluated relative to the risk of HTHA.

Early stages of voids and micro-fissuring can be difficult to find by NDE techniques. Ultrasonic testing (UT) is currently the primary method for identifying HTHA in the early stages. Depending on the equipment detection limit and location of inspection, HTHA can be found. A detailed mechanical integrity inspection plan should be executed by experienced technicians using the proper techniques and equipment. For more details, see API RP 941, Appendix E [1].

If indications of HTHA are found, a fitness for service evaluation shall be conducted and next steps determined based upon that evaluation. For more information regarding fitness for service, see API RP 579-1/ASME FFS-1, *Fitness-For-Service (FFS)* [8]. If no defects are found, future inspections should be conducted in accordance with the mechanical integrity program.

9.1 Inspection locations

Inspection of a range of exposed sections of the equipment should be planned. Consideration should be given to plain shell/pipe sections, joining welds, rolled geometries, branches, nozzles, and other areas of high stress. Each equipment item or piping section shall be individually evaluated to determine the inspection locations.

Normally high stressed areas are more susceptible to HTHA than low stressed areas. Nozzle welds, dissimilar material welds, welds with significant peaking, welded internal attachments, and areas opposite external attachments are some of the areas where high residual stresses are present.

9.2 Recommended inspection techniques

To ensure that the onset of HTHA can be detected, multiple inspection techniques should be used. Internal inspection techniques are preferred because HTHA initiates from the process side, but internal inspection is not always possible or practical. API RP 941, Annex E provides details on inspection methods for detection of HTHA [1]. The annex provides tables that summarize the advantages and limitations of each inspection method. While UT methods are identified as the most effective for detecting internal HTHA damage, two or more inspection methods are often used in combination to overcome the limitations of any single method. The selection of inspection methods and frequencies for HTHA in specific equipment or applications is the responsibility of the user. An additional resource is RR1134, *Maintaining the integrity of process plant susceptible to high temperature hydrogen attack. Part 2: factors affecting carbon steels* [9].

A summary of the most common techniques is provided in the subsequent sections. However, inspection techniques are continually evolving and the following list is not exhaustive. For all techniques, it is critical to ensure that surfaces have been suitably prepared to meet the requirements of the method being used and hence provide reliable results.

9.2.1 Ultrasonic testing

If internal inspection is not possible, then external inspection by UT can be used. There are several UT inspection techniques and equipment to identify early stages of HTHA. To conduct the most reliable inspection, information pertaining to the equipment as far as geometry, material of construction, or internal lining and location are required. Experienced NDE technicians certified in evaluating HTHA shall be utilized.

Some of the current techniques for detecting early stages of HTHA are time of flight diffraction (TOFD), phased array UT, full matrix capture (FMC) and total focusing method (TFM). These advanced techniques allow the inspector to differentiate between fabrication defects and HTHA damage. These techniques also allow for data recording, which enables comparison of inspection results over time. Other UT techniques are also available, not all of which allow for data recording. The inspection technique(s) used shall be agreed upon between the end user and the NDE company.

9.2.2 Dye penetrant testing or wet fluorescent magnetic particle testing

Dye penetrant testing (PT) or wet fluorescent magnetic particle testing (WFMPT) can be used on the internal surfaces to find HTHA damage in the form of surface cracks. However, initial stages of HTHA (decarburization, voids, and fissures) and subsurface damage cannot be detected. Also, the depth of HTHA damage cannot be determined by PT or WFMPT.

9.2.3 Field metallography and replication

In situ metallography can be used on the internal surface to detect HTHA both in the initial stages (decarburization, voids, and fissures) and in the advanced stages (cracks). Field metallography can only detect HTHA on the surface. The depth of HTHA cannot be determined.

9.2.4 Metallography

Where further quantification or verification of HTHA damage is desired, a scoop sample or section can be taken from the most susceptible area and metallographic examination performed. In cases where the internal surface is not accessible and UT is not effective, the only option to check for HTHA is to take a scoop sample or cut a section of the affected equipment/piping and perform metallographic examination in a laboratory. Metallographic examination provides the most detailed analysis, allowing the depth, stage, and extent of HTHA to be determined.

9.3 Inspection companies

The selected NDE company and inspector should have suitable experience with the type of inspection being performed. For UT inspection, experienced NDE technicians certified in evaluating HTHA shall be utilized. Certification for HTHA includes, but is not limited to:

- experience with multiple inspection techniques;
- validation of competency on test pieces with different stages of HTHA;
- testing on base material as well as weld joints; and
- demonstrating the ability to differentiate HTHA from other material defects.

9.4 Incomplete inspection

The actual scope of inspection achieved can vary from that originally specified. Practical on-site issues such as access, surface preparation, time, and component geometry can limit inspection scope. Any such limitations should be recorded, and the impact of reducing or changing inspection scope should be risk assessed by subject matter experts.

9.5 Inspection results

The inspection results shall be reviewed, and relevant information should be collected to perform a fitness-for-service evaluation by appropriate subject matter experts. If the inspection finds no relevant indications, the equipment/piping is fit for service, and the inspection program should be updated and continued. Subject matter experts should determine what future HTHA inspections are required. If the inspection finds relevant indications, then these indications shall be evaluated to determine what actions are necessary for continued operation and to develop necessary future inspection plans. Alternately, it could be necessary to stop operation and conduct immediate repair or replacement, and the inspection program should be updated accordingly.

10 References

Unless otherwise specified, the latest edition shall apply.

[1] API RP 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*, American Petroleum Institute. www.api.org

[2] CSB Report 2010-08-I-WA, May 2014, *Tesoro Refinery Fatal Explosion and Fire*, U.S. Chemical Safety and Hazard Investigation Board. www.csb.gov

[3] API RP 571, *Damage Mechanisms Affecting Fixed Equipment in the Refining Industry*, American Petroleum Institute. www.api.org

[4] API RP 581, *Risk-Based Inspection Technology*, American Petroleum Institute. www.api.org

[5] API RP 584, *Integrity Operating Windows*, American Petroleum Institute. www.api.org

[6] CGA P-11, *Guideline for Metric Practice in the Compressed Gas Industry*, Compressed Gas Association. www.cganet.com

[7] EIGA Doc 202, *Mechanical Integrity of Syngas Outlet Systems.* www.eiga.eu

[8] API RP-579-1/ASME FFS-1, *Fitness-For-Service (FFS)*, American Petroleum Institute. www.api.org

[9] RR1134, *Maintaining the integrity of process plant susceptible to high temperature hydrogen attack. Part 2: factors affecting carbon steels*, Health and Safety Executive. www.hse.gov.uk