Question 15: What practices and modifications have you implemented in response to the new High Temperature Hydrogen Attack (HTHA) guidelines and updated Nelson curves?

JOE RYDBERG (CITGO)

The primary source document for dealing with High Temperature Hydrogen Attack (HTHA) is API Recommended Practice 941 – Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants. This document provides the basic guidelines for determining the risk of HTHA in equipment that operates at elevated temperatures. At elevated temperatures and pressures experienced in refining operations, hydrogen at the surface of a metallic interface will be first adsorbed and then absorbed into steel. Diffusivity into steel is highly dependent upon a number of factors including: microstructure, alloying elements, and current temperature. Upon entering the steel, hydrogen can react with carbon or carbides to form methane. Methane, being too large to permeate through the steel is trapped in the microstructure, leading to the numerous damaging effects collectively known as High Temperature Hydrogen Attack leading to internal decarburization, fissuring, and eventually cracking. API 941 summarizes the results of experimental tests and actual data acquired from operating plants to establish practical operating limits for carbon and low alloy steel in hydrogen service at elevated temperatures and pressures. This API Recommended Practice does not address the resistance of steels to hydrogen at lower temperatures (below about 400ºF), where atomic hydrogen enters the steel as a result of corrosion or by electrochemical mechanisms.

The document contains a graph that shows the Nelson curves for carbon steel and low alloy steels. These curves are used to determine the risk of HTHA occurring in various grades of steel. This curve has been moved to lower hydrogen partial pressures and temperatures throughout the years as more industry data has come in. If you plot the temperature and partial pressure of hydrogen for the process on this graph and the point plotted is below the specified metallurgy's curve, HTHA will not occur. This graph also shows that HTHA doesn't occur at hydrogen partial pressures below approximately 50 psia, except at extremely elevated temperatures. Also shown on this graph is a curve for C-½Mo that was formerly used in the industry. However, several failures have occurred in C-½Mo equipment below this curve. After a number of failures occurred, API decided that the C-½Mo curve should no longer be used, and instead it was required that the carbon steel curve be used for C-½Mo. The newest edition of API 941 does contain a section that deals specficially with C-1/2Mo equipment, which takes into account a number of fabrication methods and testing data to determine the resistance of the material for analysis.

While 400ºF is the common deciding parameter for the threat of HTHA, 350ºF was taken to be the alarm temperature in order to have a more conservative safety factor during the initial screening of equipment and piping at CITGO Lemont. If a piece of equipment or piping was noted to be operating above this temperature, its temperature history was investigated to see if thermal excursions occur that could potentially lead to HTHA. After the equipment that operates above 350ºF criteria was established, the hydrogen partial pressure was obtained from Operations for these areas. Using these two pieces of information, the conditions for this piece of equipment were plotted on the Nelson Curve for their particular metallurgy. Potential for HTHA was then determined for that piece of equipment from the location on the Nelson Curve.

Most of the piping near the new Nelson curves has been replaced in the past with an alternate metallurgy, though there are some that still fall near, but below the curve. If operating above the curves, then replacement is suggested on the next turnaround opportunity. All vessels composed of C-1/2Mo material were replaced pre-emptively, rather than continue to inspect using uncertain techniques.

Current Nelson Curves in API 941, 216 Edition.

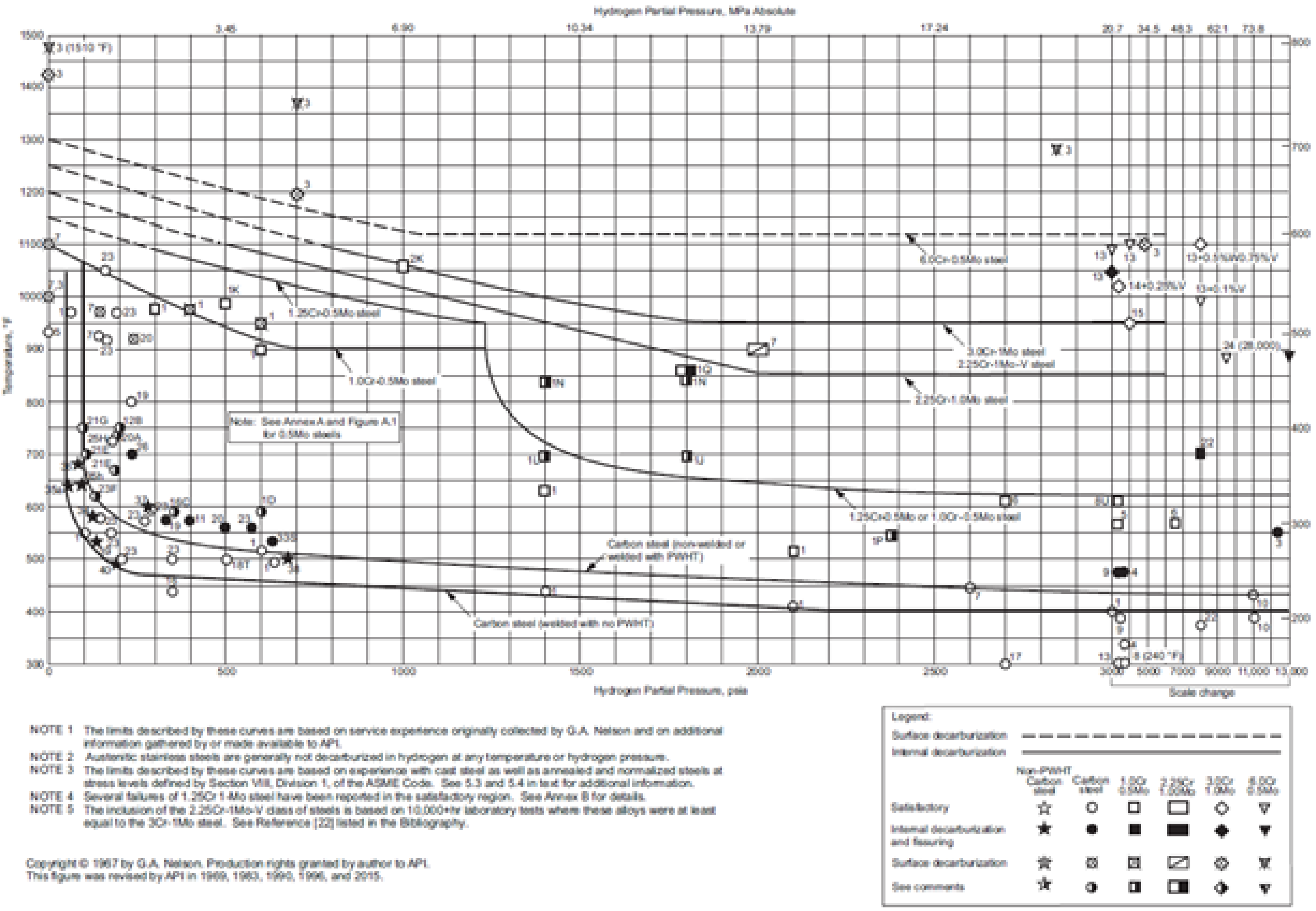

Figure 1—Operating Limits for Steels in Hydrogen Service to Avoid High Temperature Hydrogen Attack

ROBERT STEINBERG (Motiva Enterprises)

API Recommended Practice 941 "Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants" was updated in 2016 with a new Nelson curve for non-PWHT carbon steel. The new non-PWHT curve is about 50°F lower than the old curve that is still used for non-welded or PWHT carbon steel.

The new Nelson curve is used the same way as the old curve. Many refiners limit their maximum operating temperature to 50°F below the curve.

Once the new curve was in place it was necessary to review all carbon steel lines and equipment in hydrogen service. For non-welded and welded with PWHT steel there was no change. For areas where the new Nelson curve had to be applied the following options were utilized:

- For equipment that was still operating safely below the new Nelson curve no changes were needed. If there was a high temperature alarm to keep from exceeding the Nelson curve it was adjusted.
- For equipment that was operating relatively close to the Nelson curve limit, additional monitoring was put in place to ensure temperatures remained in an acceptable range. In some situations, additional thermocouples were added, generally a strap on skin thermocouple, to allow continuous monitoring. Alarms were also configured and operating procedures updated to ensure temperatures stayed below the Nelson curve.
- In a limited number of circumstances, it may be necessary to upgrade metallurgy (generally changing from carbon steel to 1¼Cr – ½Mo) to stay below the Nelson curve. Where this is needed, additional monitoring and risk assessments are performed until the equipment can be upgraded.

LARS JORGENSEN (Haldor Topsoe)

The new API-941 guidelines, from February 2016, have been implemented regarding material selection, and any carbon steel now requiring PWHT will be specified as such. Generally, this has not been a major cost issue since many clients already specify PWHT requirements on all high-pressure carbon steels.

MAX LAWRENCE (Shell Global Solutions)

In existing facilities, equipment and piping operating above the revised Nelson Curves have been identified and scheduled for inspection and evaluation. Shell's evaluation applies a safety factor on the Nelson Curves. If inspection reveals that HTA is present, the piping or equipment is identified for replacement at an appropriate priority. If HTA is not present, the inspection for HTA will be repeated periodically.

For new facilities, the established material selection protocols are followed using the revised Nelson Curves.

CHRIS WOZANIAK (Honeywell UOP)

UOP is a sitting committee member of API 941. In 2012, UOP implemented the use of post weld heat treatment (PWHT) on carbon steel operating slightly below the API 941 7th edition carbon steel curve. In 2016, API 941 released the 8th edition, which contained a new curve for carbon steel, and the existing carbon steel curve was designated as carbon steel plus PWHT. Since 2016, UOP has been exclusively using the 8th edition of API 941. Historically, UOP has always been conservative for specification of materials in high temperature, high hydrogen partial pressure environments by not setting metallurgy using operating conditions. UOP has always used the design temperature and hydrogen partial pressure set by the design pressure (H2pp = DesP * mol% H2), which provides additional safeguard when picking metallurgy that is resistant to high temperature hydrogen attack (HTHA).

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