
Question 43: In reforming units, what equipment could be susceptible to high temperature hydrogen attack (HTHA)? How are panelists approaching evaluation and replacement of equipment that could be susceptible to HTHA?

KOONTZ (HollyFrontier)

First, a little background: API 941 discusses high temperature hydrogen attack. At low temperatures, less than about 430°F, carbon steel has been used successfully up to 10,000 psi. But with elevated temperatures, the molecular hydrogen will dissociate into atomic hydrogen, which can readily enter and diffuse into the steel. The hydrogen reacts with the carbide in the steel to form methane, which is trapped inside the steel and will eventually form a crack or blister. The addition of carbide stabilizers to the steels – such as chromium, molybdenum, tungsten, and vanadium – can resist the decarburization reaction within the steel.

Beginning in the 1940s, G.A. Nelson collected and published empirical curve data to demonstrate the conditions at which high temperature hydrogen attack is expected for specific metallurgy and operating conditions. These data are known as the Nelson Curves and have been continuously updated over the years to include additional failures due to HTHA. The Nelson chart originally included a curve for carbon-0.5 moly (molybdenum), which was midway between the carbon steel curve and the 0.25 chrome-0.5 moly curve. Ever since 1970, a series of unfavorable service experiences with carbon-0.5 moly steels have reduced confidence in the position of its curve on the chart. Data indicate that how the metal is fabricated does have a strong correlation to its susceptibility to HTHA. In 1990, API removed the carbon-0.5 moly curve completely from the Nelson chart.

HTHA

- **API RP 941 discusses High Temperature Hydrogen Attack (HTHA) extensively**
- **High temperature causes H₂ to dissociate**
 - Atomic H diffuses into metal
 - H reacts with carbide to form CH₄ (Decarburization)
 - Trapped CH₄ causes blister or crack
- **Nelson curve data have been collected and added to the graph since the 1940's**
 - Acceptable operating ranges for different metals based on experience

HollyFrontier generally uses the carbon steel curve on the Nelson chart to evaluate carbon-half moly steels in its process units. Some process equipment has utilized stainless steel cladding or weld overlay to mitigate the concern with HTHA of the base metal. However, this does not completely eliminate the risk. Hydrogen will still diffuse through the cladding and affect the base metal. The partial pressure of the hydrogen at the base metal will be lower than without the cladding, but it must be carefully evaluated to

assure that HTHA would not be expected. Real-world experiences have also demonstrated that no cladding or weld overlay is perfect. It only takes one small imperfection for the hydrogen to find the base metal and attack it. API says that it is not advisable to take credit for the presence of a stainless-steel cladding overlay when selecting the base metal for a new vessel.

HTHA

- **API 941 removed C-0.5Mo curve from chart in 1990 to reflect notable failures in industry**
- **Stainless steel cladding / overlay mitigates HTHA of base metal, but does not eliminate**
 - Requires detailed engineering analysis of each vessel to determine fitness-for-service
- **Inspection requires advanced techniques to detect HTHA before mechanical integrity is affected**

HollyFrontier has performed a full review of its process units to identify the risk for HTHA, especially for carbon-0.5 moly steels. The review indicated concerns in the reaction section of some of the units. The general strategy for HollyFrontier for carbon-0.5 moly steel operating above the carbon steel Nelson

Curve is to remove it from service. If the carbon-0.5 moly steel is clad or overlaid with 300 series stainless steel, a Fitness for Service Evaluation is performed to ensure that the equipment is safe for operation.

QH43



HTHA

- **API 941 removed C-0.5Mo curve from chart in 1990 to reflect notable failures in industry**
- **Stainless steel cladding / overlay mitigates HTHA of base metal, but does not eliminate**
 - Requires detailed engineering analysis of each vessel to determine fitness-for-service
- **Inspection requires advanced techniques to detect HTHA before mechanical integrity is affected**

One example is of a naphtha hydrotreater that was operating slightly above the carbon steel Nelson Curves. Based on a detailed analysis of the cladding, it was deemed acceptable for continued operation. We are, though, in the process of a project to replace that reactor.

QM43



HTHA

- **General strategy of HF is to remove C-0.5Mo equipment from service if operating above CS Nelson curve**
 - Fitness-for-service evaluation is performed if clad / overlaid with 300 series SS
- **Example 1: NHT reactor (C-0.5Mo with 300 series cladding) operating above CS Nelson curve**
 - Engineering analysis deemed fit-for-service
 - Project in progress to replace reactor

In another example, a kerosene hydrotreater operates in two distinct regimes. It makes ULSK (ultra-low sulfur kerosene) part of the time and jet the rest of the time. While operating in the jet regime, the operating point is below the carbon steel Nelson Curve and is, therefore, not a problem. However, when we operated in the high severity mode, it did go above the carbon steel curve. Since the analysis was performed, we no longer run the high severity operation, and there is a project underway to replace that reactor.

Q413

HTHA



- **Example 2: DHT reactor (C-0.5Mo with 300 series cladding) operating above CS Nelson curve**
 - High severity mode above curve, low severity below curve
 - Decision made to halt high severity operation
 - Project in progress to replace reactor

The original question asked about reformers. Older semi-regen reformers are especially of concern since they operate at much higher hydrogen partial pressure than does a modern CCR. HollyFrontier operates two semi-regen reformers in El Dorado and Woods Cross. These reformers have unusually high reactor pressures for reducing coking. Of course, there is concern about both the feed effluent and the reactor circuits. The review did not indicate any carbon-0.5 moly steel in the reformers. However, in one case, it was found that at end-of-run conditions, the operating points were touching the 1.0 chrome-0.5 moly curve for a particular vessel. Historical data was used to determine how much time had been spent touching the "curve." This data was then used to perform a detailed Fitness for Service Evaluation, and the reactor was deemed "fit for service". Future inspections will utilize advanced nondestructive evaluation (NDE) on these areas to increase our confidence that HTHA is not impacting the integrity of the vessel.

HTHA

- **Example 3: Semi-Regen reformer reactor circuit (1Cr-0.5Mo) “touching” Nelson curve at end-of-run**
 - Engineering analysis deemed fit-for-service
 - Future inspections will utilize advanced techniques to monitor the system

KOONTZ (HollyFrontier Corporation)

High temperature hydrogen attack (HTHA) is discussed extensively in API Recommended Practice 941. At low temperatures (less than ~430°F), carbon steel has been used successfully at pressures up to 10,000 psi. However, at elevated temperatures, molecular hydrogen will dissociate into atomic hydrogen

which can readily enter and diffuse through steel. The hydrogen reacts with the carbide in the steel to form methane, a process termed decarburization. The methane is too large to diffuse out of the steel and eventually the internal pressure is high enough to cause a blister or fissure in the steel. These cracks eventually result in a significant deterioration of mechanical properties which can cause a loss of containment. The addition of carbide stabilizers to the steel such as chromium, molybdenum, tungsten, vanadium and titanium resist the decarburization reaction within the steel.

G.A. Nelson collected and published empirical data for API beginning in the 1940s to demonstrate the conditions at which HTHA is expected for specific metallurgy and operating conditions (temperature and hydrogen partial pressure). These data are known as the Nelson curves and have been continually updated over the years to include additional failures due to HTHA. The Nelson chart originally included a curve for C-0.5 Mo (carbon-0.5 moly) that was midway between the CS (carbon steel) curve and the 1.25 Cr (chrome)-0.5 Mo curve. Since 1970, a series of unfavorable service experiences with C-0.5 Mo steels has reduced confidence in the position of its curve on the chart. Data indicate that how the metal is fabricated has a strong correlation to its susceptibility to HTHA. In 1990, API removed the C-0.5 Mo curve completely from the Nelson chart. HollyFrontier generally uses the CS curve on the Nelson chart to evaluate C-0.5 Mo steel in its process units.

Some process equipment has utilized stainless steel cladding or weld overlay to mitigate the concern with HTHA of the base metal. However, this does not eliminate the risk completely. Hydrogen will still diffuse through the cladding and affect the base metal. The partial pressure of hydrogen at the base metal will be lower than without the cladding, but it must be carefully evaluated to assure that HTHA would not be expected. Real world experience has also demonstrated that no cladding or weld overlay is perfect; it just takes one small imperfection in the cladding/overlay to allow full hydrogen pressure to impact the base metal. Furthermore, inspection of the base metal is difficult as it is hard to find the damage below the cladding/overlay before enough damage has been done to decrease the mechanical strength. API says that it is not advisable to take credit for the presence of a stainless-steel cladding/overlay when selecting the base metal for a new vessel (i.e., overlay/cladding would be used to resist other corrosion attacks, but not HTHA).

HF has performed a full review of its process units to identify risks for HTHA (especially for C-0.5 Mo steel). The review indicated concerns in the reaction section of some of the units. The general strategy of HF for C-0.5 Mo steel operating above the CS Nelson curve is to remove it from service. If the C-0.5 Mo steel is clad overlaid with 300 series stainless, a fitness-for-service evaluation is performed to ensure that the equipment is safe for operation. In one example, a naphtha hydrotreater is operating slightly above the CS Nelson curve. Based on a detailed analysis of the cladding it was deemed acceptable to continue operation. However, HF is in the process of replacing the reactor and part of the feed/effluent circuit to assure long term reliability.

In another example, a kerosene hydrotreater operates in two distinct regimes when its product switches between jet and ULSK/ULSD (ultra-low sulfur diesel). It is below the CS Nelson curve when producing jet, but it passes above the curve when producing product at 10 ppm sulfur. Since the HTHA analysis has been completed HF no longer runs the unit in high severity mode. A project is underway to restore the ability to operate in high severity mode. The original question asked about reformers. Older semi-regeneration reformers are especially of concern since they operate at much higher hydrogen partial pressures than a modern CCR. HF operates two semi-regeneration reformers in El Dorado and Woods

Cross that have unusually high reactor pressures to reduce coking. Of course the main areas of concern are from the feed/effluent exchanger(s) through the reactors and furnaces. The review did not indicate any C-0.5 Mo steel in HF reformers. However, in one case it was found that at end-of-run conditions the operating points were “touching” the 1 Cr-0.5 Mo Nelson curve. Historical data was used to determine how much time has been spent “touching” the curve. This data was used to perform a detailed fitness-for-service evaluation. Future inspection will utilize advanced NDE on these areas to increase confidence that HTHA is not impacting mechanical integrity.

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