Question 3: How are you managing your units to mitigate risk of HTHA (High Temperature Hydrogen Attack)? What are monitoring best practices? Should we be concerned about short term operating periods such as startup, shutdown, hot stripping, etc.?

Minh Dimas (CITGO)

HTHA is a form of degradation of metal caused by hydrogen reacting with carbon in the metal to form methane in a high temperature environment, typically above 400 deg F and 50 psia H2 partial pressure. The methane gas accumulates in the grains and voids and expands to form blisters. This weakens the metal strength and initiates cracks in the metal. Alloys of particular concerns are carbon steels, ½-Mo and ½-Mn steels, and 1-Cr alloy.

We evaluate all of our hydrotreaters for HTHA, using normal operating data and short-term excursion data (such as hot H2 strip). We plot the H2 partial pressure and temperature on the Nelson Curves to determine the likelihood for HTHA to occur. Most of our equipment operates on the safe side of the Nelson curves due to higher alloys. For equipment with C-½ Mo material, we increase the inspection frequency to look for HTHA, which may be difficult to detect with conventional NDE and may required specialized techniques for early detection. We also plan to upgrade the metallurgy of an exchanger that has a carbon steel channel head but clad with stainless steel.

Martin Gonzalez (BP)

API Recommended Practice no. 941 “Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants” gives the well-known Nelson curves against which temperature and hydrogen partial pressure of equipment can be evaluated. It is common in the industry to apply safety margins of up to 50 deg F on temperature and 25-50 psi on hydrogen partial pressure.

Installing temperature instrumentation between shells or channels of heat exchanger banks in high pressure hydrogen service may be helpful for providing assurance that conditions do not fall above the Nelson curves. Fouling should be taken into account as it may result in significantly different operating temperature than assumed in design. Consideration should also be given to transient operating conditions such as when taking one of a pair of exchangers out of service, opening or closing bypasses, and periods of operation with hydrogen-only, as this may cause temperatures to increase to a level above the Nelson Curve. Consider also replacing C-½ Mo piping with higher alloy steels.

Shankar Vaidyanathan (Flour)

For older reactors, especially those in service beyond their initial design service life, a good risk management approach is to investigate whether the cumulative time spent at the short-term conditions falls below the HTHA incubation curves. Refiners maintain a database of equipment and piping operating close to HTHA conditions. This is used in fatigue evaluation studies, equipment and piping recertification, remaining life analysis, and to set inspection priorities while defining long-term maintenance needs. In some cases, study has shown that replacement of C-½ Mo with upgraded material is justified. Positive material identification procedures will help to avoid improper material substitution at turnarounds. Ensure technical reviews of metallurgy, operating pressure and temperature alarm settings when a unit is recertified for use under conditions different from the original design.

Tim Lewer (Shell)

HTHA is a function of hydrogen partial pressure, temperature, and metallurgy.

1. Reactor Effluent Train – The effluent train must have the proper design to ensure temperatures are below HTHA temperature prior to any metal spec change. Be aware of creep, where-by process improvements, debottlenecking, and heat integration changes can move the HTHA critical temperature downstream past the metal spec change (i.e., 1¼ Cr changes to carbon steel).

2. HTHA is time dependent – Longer exposure to temperatures above the Nelson curve will increase the risk.

3. Abnormal periods – All unit conditions must be evaluated for risk of HTHA. Create a spreadsheet with all piping or equipment that is above the HTHA pressure. Define the maximum temperature and maximum hydrogen partial pressure cases, and evaluate versus the Nelson curve. Log the instruments used to monitor the unit temperatures and pressures and create appropriate alarm limits or operating procedures.

Tags

[Fouling]

[Heat Exchangers]

[Hydrogen]

[Process]

Reactor Vessel

Safety

Start-up

Year

2011