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Baker Engineering and Risk Consultants, Inc. is one of the world’s leading explosion analysis, structural design, and risk engineering companies. BakerRisk provides comprehensive consulting, engineering, laboratory and range testing services to government agencies and private companies who are involved with dangerous, highly hazardous, reactive, or explosive materials.

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AVOIDING HIGH TEMPERATURE HYDROGEN ATTACK

Has equipment deteriorated due to elevated temperature exposure in the presence of hydrogen? This question is frequently asked by those in ammonia, refinery, and chemical plants, who use piping, heat exchangers, and pressure vessels containing hydrogen at elevated temperatures. Beginning with research performed in the 1940s, equipment exposed to hydrogen at elevated temperatures is known to potentially degrade over time by a process called high-temperature hydrogen attack (HTHA). This technical brief discusses some necessary safety considerations and controls used by plant designers and operators to reduce the risk of failure of such equipment.

HTHA Phenomenon
High-temperature exposure of the carbon and low-alloy steels used for piping and pressure vessels in high-pressure hydrogen service leads to a special form of degradation known as HTHA, sometimes called hydrogen attack. This is not the same as hydrogen embrittlement which degrades toughness at low temperatures. HTHA leads to degradation of material properties at elevated operating temperatures and can result in sudden and catastrophic brittle failure.

Under certain temperature conditions and hydrogen partial pressures, atomic hydrogen permeates the steel and reduces iron carbide (Fe3C) in the steel to form methane (CH4), causing fissuring between grains (compare the undamaged sample shown in Figure 1(a) with the hydrogen-damaged sample shown in Figure 1(b)). In fissuring, the ductility of the metal is significantly and permanently lowered. The severity of hydrogen attack increases with increasing temperature and hydrogen partial pressure.

HTHA Standard
The operating limits for steels can be empirically described using the operating temperature and the hydrogen partial pressure, as originally discussed by Nelson in 1949 and in API recommended practice (RP) 941, “Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants.” Since the 1970s, empirical data have been collected from operating plants and tests to establish operating limits for carbon steel and low alloy steel equipment in hydrogen service at elevated temperatures. Using API RP 941 as a guide, if a piece of equipment or piping is operated above the API RP 941 (Nelson) curve, then the material is not suitable for service under those conditions. For example, if the normal operating conditions are a temperature of 288 °C (550 °F) and 13.79 MPa (2,000 psig) hydrogen partial pressure, as illustrated in Figure 2, the carbon steel is not suitable for service under those conditions.
Either the temperature or pressure would have to be reduced below the carbon steel curve, or chromium alloyed steel should be considered for use instead. The selection of a $1\frac{1}{4}$ Cr- $\frac{1}{2}$ Mo material would be the preferred choice.

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**Operating Conditions**
To adequately assess HTHA susceptibility, both the actual conditions of exposure for the metal wall and the operating conditions of the equipment must be known. Typical or possible design limits are not adequate to assess HTHA susceptibility. A good HTHA assessment requires validation of data with process engineering involvement and actual field data. In determining the actual conditions, the placement of temperature and pressure indicators is important, as well as knowing whether process creep conditions have occurred over a period of time. Once the HTHA limits are determined, safe operating limits with necessary process alarms should be in place, and a response plan should be implemented for safe operations when those limits are exceeded.

**Lined Equipment**
For corrosion purposes, vessels may be clad, lined, or weld overlaid to protect the vessel surface, provided hydrogen does not diffuse through the liner or migrate behind the lining or cladding. If that occurs, then the vessel wall may be susceptible to HTHA. Refractory lining is often used to insulate a pipe or vessel to lower the metal wall temperature and is an effective way to reduce the effects of HTHA. If the refractory degrades, cracks, or deteriorates due to operating conditions or flexure of the refractory, hot spots can form which would increase the metal wall temperature and possibly exceed the HTHA operating limits of the equipment, as shown in Figure 3. This figure shows how a degraded refractory and hot spot could result in exceeding the operating temperature limit for a carbon steel line.

**Summary**
With proper safety considerations and controls, the risk of HTHA failures can be greatly reduced. The following practices should be considered:

1. Selecting the proper material for the operating conditions, and for increased temperatures, considering the use of alloys with higher weight percentages of chromium and molybdenum.
2. Using actual operating temperatures for assessing HTHA susceptibility, and validating that the actual operating temperatures and pressures are below the API 941 curve by a defined amount.
3. Employing experienced individuals who understand the HTHA phenomenon and API RP 941 recommended practices.
4. Performing regular process hazard assessment of the operating conditions including changes in pressure, temperatures, or partial pressure of hydrogen.
5. Verifying the actual operating conditions the equipment experiences through good field data.
6. Locating pressure and temperature sensors so they measure the actual conditions of equipment that could be susceptible to HTHA.
7. Determining whether process creep has occurred.
8. Evaluating material or operating changes using a management of change (MOC) process.
9. Evaluating if temperature excursions and regeneration operations affect HTHA susceptibility.
10. Providing definite safe operating limits with necessary process alarms and a response plan when those limits are exceeded.
11. Performing regular infrared inspections, especially on refractory-lined equipment.
12. Ensuring that the operating limit is understood, and appropriate actions are taken if exceeded.
13. Ensuring that proper foundation support for refractory-lined equipment is present to reduce flexure of the refractory.
14. Selecting inspection methods and frequencies to detect initial stages of HTHA.
15. Ensuring that written procedures are in place and implemented to provide guidance on inspections and intervals.
16. Knowing the history of the equipment, and if unknown, making sure that HTHA inspections are performed.
17. Performing PMI regularly, especially during installation, welding, and maintenance operations.
18. Documenting all findings in an inspection program and implementing follow-up with appropriate actions.