California Emphasis Program

California Refining Industry

Naphtha Hydrotreater Units

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California Emphasis Program – Naphtha Hydrotreater Units

On April 6, 2010, a tragic accident occurred at the Tesoro Refinery in Anacortes, WA, in the Naphtha Hydrotreater process unit (NHT). During routine operations involving an on-line switching of unit heat exchanger feed trains, seven employees were killed immediately, or died later of thermal burn injuries sustained when a feed-effluent heat exchanger catastrophically failed due to high temperature hydrogen attack (HTHA), releasing a hot, pressurized flammable hydrocarbon/hydrogen mixture which ignited. Tesoro released its investigative results to the media on September 01, 2010.

Rather than await the final report, the Northern and Southern California Process Safety Management district managers proactively initiated a California Emphasis Program (CEP) in April, 2010, under which Program Quality Verifications (PQV) were conducted in every California petroleum refinery to examine each refiner's procedures and practices for identifying and mitigating corrosion damage known to be produced in the NHT process environment. The PQV focused on the NHT process units in general, and on NHT feed-effluent heat exchangers in particular. At the time the CEP began, the exact cause of the heat exchanger failure in Anacortes was yet unknown.

What was known based on the documented historical experience of the refining industry, and published in its own technical literature is that the NHT operating environment can increase process equipment susceptibility to various forms of chloride corrosion and hydrogen attack.

The NHT process unit removes sulfur and nitrogen from straight run naphtha downstream of the Crude Distillation process unit (CDU). Removing these impurities involves treating the naphtha with hydrogen to create a suitable feed stock. The process poses operating and mechanical integrity challenges due to the presence of inorganic salts such as sodium chloride, magnesium chloride, and calcium chloride. Hydrogen is absorbed into metal, becomes trapped, and can cause embrittlement, cracking, and blisters.

While each refiner operates its NHT differently consistent with defined business objectives, a feed-effluent heat exchanger nevertheless serves essentially the same purpose throughout the refining industry. Namely, to transfer the heat produced in a reactor pressure vessel to a feed stock. Typically, NHT feed-effluent exchangers are designed with consideration for potential *sulfidation*, *high temperature H_2/H_2S corrosion*, *ammonium chloride corrosion*, and *high temperature hydrogen attack*.

Additional corrosion phenomena found in the NHT include *ammonium bisulfide* and *hydrochloric acid corrosion*. Chlorides are difficult to control, and various types of aggressive corrosion phenomena present at varying operating temperatures and pressures downstream of the CDU.

Salt corrosion is caused by the hydrolysis of some metal chlorides to hydrogen chloride (HCl) and the subsequent formation of hydrochloric acid when crude is heated. Hydrogen chloride may also combine with ammonia used in chemical injection to form ammonium chloride (NH_4Cl), which causes fouling and corrosion.

Sulfur and nitrogen compounds are converted by a catalyst in the first stage reactor to hydrogen sulfide and ammonia. As the effluent stream from the reactor cools down, the ammonia and hydrogen sulfide combine to form solid ammonium bisulfide (NH_4HS) salts. Both concentrated NH_4Cl and NH_4HS are highly corrosive to carbon steel and low alloys when wet. Dry, they are foulants that can inhibit heat transfer.

A comprehensive program for chlorides control should include monitoring of chloride levels in incoming crude in accordance with established acceptance criteria, effective desalting upstream of the CDU, effective water wash procedures and practices, effective chemical injection, appropriate materials selection and design, and rigorous monitoring.

Carbon and C-½ Mo steels in hydrogen service at temperatures above 450º F and pressures above 100 psia are susceptible to high temperature hydrogen attack (HTHA), a brittle fracture of a normally ductile material that occurs partially due to the corrosive effect of an environment. Under these operating parameters atomic and molecular hydrogen permeate the steel and react with dissolved carbides to form methane gas. The reaction decarburizes the steel, creating high localized stresses and resulting in voids and micro cracks that do not necessarily produce a tell-tale reduction in metal wall thickness.

Damage to welds, weld heat affected zones (HAZ), and/or base metal is undetectable by conventional nondestructive examination methods during an incubation period during which time methane pressure builds in submicroscopic voids. HTHA is a long-term corrosion phenomenon that can be selective in location and degree of damage.

These corrosion phenomena are generally well understood, along with the mechanisms by which they degrade process equipment. Detection of each type of corrosion can be elusive given variability in process operating conditions, limitations in the monitoring equipment, and difficulty interpreting the data gathered.

The Northern and Southern California PSM district offices performed PQV compliance inspections in 11 refineries throughout California. On average, the NHTs had been in service from 25 to over 30 years. In every facility the metallurgy in its NHT(s) had been upgraded over time both in response to, then in anticipation of the effects of the types of corrosion discussed earlier.

The CEP focused on a review of each employer's inspection, maintenance and operating procedures, practices, and experience specific to NHT feed-effluent heat exchangers. The Compliance personnel who conducted the inspections anticipated that these data collectively would chronicle equipment failures, near misses, and degradation. And that each facility's historical record would reflect an evolving understanding of NHT corrosion phenomena and their control.

The Inspectors expected to find documentation of the effects of hydrogen-induced damage, HTHA, and chloride corrosion in equipment whose metallurgy was vulnerable in an operating environment now processing sourer, higher acid crude slates, and more “opportunity crude”, which contains higher levels of contaminants and water. And they expected to find appropriate administrative, operational, and technical responses to the challenges presented. Such responses should include increased inspection, process changes, operating procedure modifications, and upgraded metallurgy. The costs of metallurgical upgrades are significant, and in some cases, facilities opted to modify process parameters and operating procedures in order to obviate “alloying up.”

Older process units used carbon steel, low chrome steels, 400 series stainless steel and non-stabilized 300 series stainless steel at temperatures higher than is considered safe today. In addition, these units used metallurgy such as C-½ Mo, which is now avoided as a result of industry experience. Operating limits for steels operating in a hydrogen environment are given in *API Recommended Practice 941 Steels for Hydrogen Service at Elevated Temperatures and Pressure in Petroleum Refineries and Petrochemical Plants.* The limits for C-½ Mo steels have been lowered twice because of unfavorable service experience; the first time in 1977.

After additional instances of HTHA occurred as much as 200º F below the revised 1977 Nelson Curve, the C-½ Mo curve was removed altogether in 1990 and its specifications became identical to carbon steel. Equipment built before 1990 operating above the Carbon Steel Curve was suddenly at risk. New or replacement equipment base materials for heat exchanger shells and nozzles should be either 1.25 Cr-0.5 Mo or 2.25 Cr-0.5 Mo based on API 941 Nelson Curves. Cladding should be 300 series stainless steel, dependent on operating temperature and presence of hydrogen.

The CEP discovered that a common practice among at least some of the major oil refiners is to permit operation at 50º F above the Carbon Steel curve for C-½ Mo equipment. However, the equipment is prioritized for appropriate assessment, inspection and maintenance based on temperature, hydrogen partial pressure, operating time, thermal history of steel during fabrication, stress, cold work, age, presence of cladding. California refiners recognize that cumulative operating time above the Nelson Curve increases equipment susceptibility to HTHA. While the equipment is in service at elevated temperature, the solubility of hydrogen in the Cr-Mo steels is higher, and the ductility of the material is greater, which prevents cracking phenomena. If temperatures are reduced at a rate which is too fast for diffusion, the diffusible hydrogen can localize at so-called trap sites such as dislocations, carbides, and non-metallic inclusions.

This can result in hydrogen "supersaturation" and hydrogen induced damage. The reduced ductility of the metal at the lower temperatures and the existence of applied, residual or thermal stresses may induce crack initiation. Such equipment must be inspected for HTHA using at least two inspection methods in combination. Base metal HTHA can be detected in its early stages using ultrasonic backscatter, velocity ratio, attenuation, and/or spectral analysis techniques. Use of ultrasonic shear wave inspection can reliably detect HTHA in welds *only after* cracks have formed. Higher frequencies can enhance detection capability.

The California Emphasis Program was initiated in response to a tragedy that, like most workplace injuries, likely could have been avoided. While it might be axiomatic that corrosion is inherent in the petroleum refining process, the direct costs of which approach $4 billion annually, the technology exists to manage its effects. The California refining industry collectively meets the challenges presented by corrosion phenomena known for decades to exist in the Naphtha Hydrotreating process.

Each Refiner has developed and implemented its own proprietary strategies for controlling the constellation of damage mechanisms common to the complexities of crude oil refining. All of these programs incorporate recognized and generally accepted good engineering practices for managing and reducing risk.

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Non-destructive Examination (NDE) Methodologies currently in use:

UT: Ultrasonic attenuation, backscatter, velocity ratio, spectral analysis & shear wave

TOFD: Time Of Flight Diffraction

IRIS: Internal Rotation Inspection System (UT immersion pulse echo)

WFMT: Wet Fluorescent Magnetic Particle Testing

PT: Penetrant Testing

MFL: Magnetic Flux Leakage

MFRC: Multiple Frequency Eddy Current

RFEC: Remote Field Eddy Current

RT: Radiography

IR: Infrared Thermography

Code References

API 570 - *Piping Inspection Code*

API 571 - *Damage Mechanisms Affecting Fixed Equipment in the Refining Industry*

API 572 – *Inspection of Pressure Vessels (see Inspection for Specific Damage Mechanisms)*

API 579 - *Fitness-For-Service Recommended Practice*

API 932 B – *Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control In Hydroprocessing Reactors Effluent Air Cooler (REAC) Systems*

API 941 - *Steels for Hydrogen Service at Elevated Temperatures and Pressure in Petroleum Refineries and Petrochemical Plants*

ASTM D4929 – *Standard Test Methods for Determination of Organic Chloride Content in Crude*

The CEP identified control measures and best practices implemented throughout the California refining industry to address corrosion phenomena in Naphtha Hydrotreater process units. These include:

Chlorides Control

- Eliminate high chloride content crudes from the slate
- Segregate high nitrogen content feeds from the NHT
- Conduct a Management of Change (MOC) for crude slate modifications
- Maintain operating temperature above salt deposition temperature
- Perform intermittent & continuous water washing, both on & offline
- Closely control wash water frequency, rate and sampling to ensure salts removal (not simply wetting)
- Routinely monitor incoming raw crude for salt and chloride content (typically 20-50 ppm chlorides and <15 ptb salts)
- Routinely monitor desalter 'salts removal efficiency'
- Maintain sludge-free desalters
- Maintain desalter electrical grids
- Avoid desalter bypassing during upset conditions
- Use 2 desalters in series to achieve greater efficiency
- Include 'note' boxes in water wash operating procedures that explain purpose & criticality of salts removal
- Address water wash & chlorides control in Process Hazard Analyses (PHA)

Inspection

- Increase inspections; consider event-driven vs time-based
- Eliminate dead legs; or closely monitor for corrosion
- Ensure low spots in piping systems are liquid free at startup
- Upgrade metallurgy
- Perform Corrosion Risk Assessments
- Perform in-situ metallography or remove material samples from equipment subject to *High Temperature Hydrogen Attack* (HTHA) for analysis
- Train inspection personnel to recognize HTHA using reference test blocks known to have HTHA damage
- Assess all carbon steel, C-½ Mo, 1 Cr, 1.25 Cr, and 2.25 Cr components for HTHA; replace all bare components or components with damaged cladding or weld overlay operating above their respective Nelson Curve limit
- Maintain a list of all C-½ Mo equipment, prioritizing inspection frequencies based on hydrogen partial pressure & temperature, thermal history of steel during fabrication, stress, cold work, age, presence of cladding
- Implement *Special Emphasis* HTHA inspection programs
- PWHT carbon steel to increase corrosion resistance
- Establish a Positive Material Identification (PMI) program to ensure susceptible components are not inadvertently installed in high alloy systems
- Establish injection & mix point corrosion monitoring program (as per API 570)
- Address criticality of Nelson Curve operating limits in PHA

Process Controls

- Adjust process limits
- Modify operating and maintenance procedures
- Minimize water carryover from high pressure to low pressure separator
- Improve water separation in fixed equipment
- Control temperatures within defined limits to ensure carbon and C-½ Mo steels never operate too close to Nelson Curve limits; or ≥50º F or ≥50 psi above the curve limits for short periods of time
- Control NH_4HS velocity and concentration within prescribed limits in REAC and piping
- Add high temperature limit alarms
- Use chemical injection: ex: ammonia, caustic, organic amine

Miscellaneous

- Implement procurement controls for materials to be used in special/severe process environments
- Restrict imported materials from suppliers whose quality control is suspect