HP | Process Optimization

Naphtha hydrotreaters: The underappreciated link between hydroprocessing and reforming—Part 1

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Some refiners consider naphtha hydrotreaters (NHTs) as the preferred hydroprocessing units to more easily support the "wide spots in the line" between the money-making crude reforming and isomerization processes. Relative to higher severity hydroprocessing units, NHTs are typically lower pressure units, with lower hydrogen (H_2) consumption, lower heat release, simpler and smaller reactors, lower operating temperatures and pressures, etc. For NHTs feeding straight-run naphtha only, less-experienced personnel will typically struggle to guess what the worst possible thing that can happen is when operating this asset.

Imagination can, unfortunately, miss the unique susceptibilities (and benefits) of operating NHTs that are distinct from most of the rest of the hydroprocessing and reforming worlds. The NHT is unquestionably a critical puzzle piece—problems with it can turn into a full refinery shutdown. This pain is most pronounced in refinery configurations with limited intermediate storage, where the reformer is the only source of H_2 and the NHT is the only source of reformer feed.

The following discusses the features of NHT operation that can result in increased risk of loss of primary containment, unreliable operation or unexpected benefits. Topics covered in Part 1 of this article include:

- Different fouling mechanisms for the feed/effluent exchanger feed and product sides, and how these can lead to unexpected risk of high-temperature H_2 attack (HTHA)
- Impacts of a fully vaporizing feed on H_2 partial pressure and HTHA susceptibility, particularly under startup, shutdown and upset scenarios
- Managing reactor feed/charge furnace coking
- Chlorides in feed streams, where they come from, and what impact they can have on pressure boundaries, heat exchange and pressure drop in the reactor loop
- The unique coking tendencies of naphtha feeds, both straight-run and cracked, and their impact on feed/effluent exchanger and reactor feed/charge furnace performance
- The impact of reactor section metallurgies selected for resistance to high-temperature H_2-hydrogen sulfide (H_2S) sulfidation, and its impact on reactor pressure drop.

Part 2 of this article, to be featured in the December issue, will cover:

- Things that may not be measured in the feed that can lead to unexpected pressure drop and catalyst activity loss
- Guard reactor purposes and benefits
- Sulfur recombination that can occur if the reactor is overfired
- Benefits of routing reformer-net H_2 through NHT H_2 makeup.

Compared to more severe hydrotreating applications, the NHT process flow is simple. **FIG. 1** is a process flow diagram of a typical hydroprocessing unit, with both feed oil and H_2 fed to the reactor feed/charge preheat furnace. For NHTs, it is the level below the process flow that drives complexity.

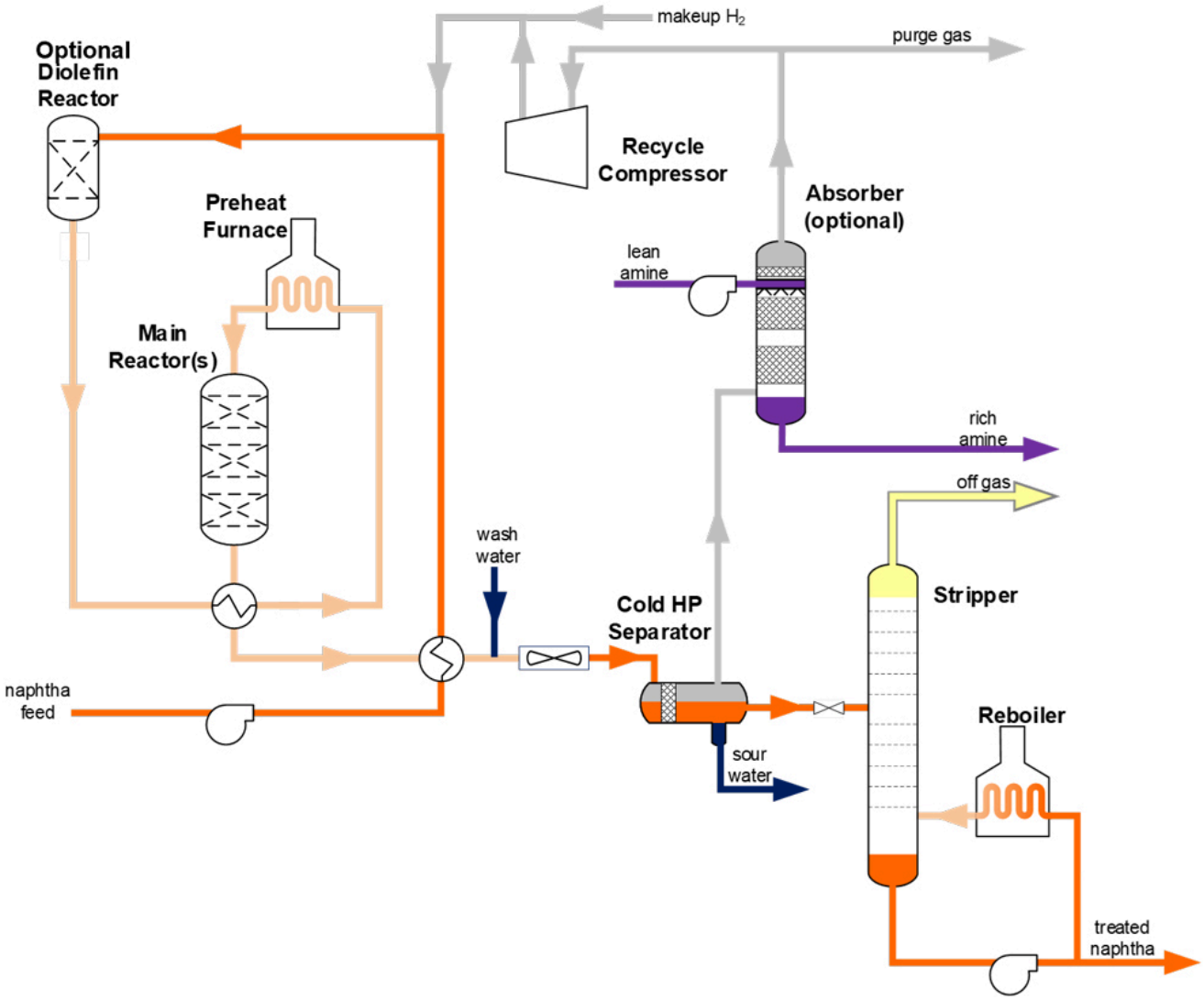


FIG. 1. Typical NHT process flow.

Let us begin with oil and gas feeds. Specific unique features and associated risks include:

- The reactor feed/charge preheat furnace and reactor typically operates with the feed oil fully vaporized at both the inlet and outlet. **Note:** This differs to units that feed diesel and heavier streams, where some liquid is always present. Full feed vaporization has pronounced impacts on the H_2 partial pressure profile in the reactor loop. With everything else being equal, oil vaporization also results in dramatically higher H_2 partial pressures when the oil vaporization reduction in H_2

partial pressure is absent during feed outages, startup and shutdown, relative to normal operations. This increases the risk of HTHA.

- The feed is typically low sulfur (< 1 wt%) and low nitrogen (< 100 ppm), which, combined with the generally lower pressures these units operate at, results in the use of carbon steel and other low-alloy metals in areas where higher severity hydroprocessing units will use high alloys and stainless steel. The presence of these low alloys increases the probability of issues related to corrosion products, and susceptibility to HTHA and acid corrosion, as detailed below.
- Naphtha is typically half the molecular weight of diesel (~100 vs. ~200), and a fourth of the molecular weight of gasoils (~400). That means when it vaporizes, it generates a lot of moles. This is critical to consider when examining H_2 partial pressure profiles and HTHA risk.
- The feeds, both oil and gas, can contain significant amounts of chlorides, and from potentially surprising sources: crude unit overhead water (if carried over), chloriding agents (such as perchloroethylene used to maintain reformer and isomerization catalyst activity) via recovered oil processing and chlorinated solvents that have made their way into the feed via crude contamination. The species formed from these chlorides—ammonium chloride (NH_4Cl) and hydrochloric acid (HCl)—are both acidic. Since there is little nitrogen in the feed relative to the chloride, only some of the chlorides will get tied up as less acidic NH_4Cl, and the balance will get hydrolyzed to strongly acidic HCl.
- Treat gas rates are relatively low. They typical range from 42 standard cubic meters of gas per cubic meter (Sm^3 gas/m^3)–168 Sm^3 gas/m^3 oil. The low gas-to-oil ratio combines with the fully vaporized, low molecular weight feed to influence the reactor loop H_2 partial pressure profile.
- The feed oil is thermally unstable and will polymerize when heated. Both the naphthas from virgin crude sources and from carbon-out upgrading processes (fluid catalytic crackers, cokers and visbreakers) contain molecules (unsaturated compounds such as thioethers, dialkyl peroxides and esters) that, when heated or exposed to H_2, can create gums. The gums, when formed, will tend to drop out and turn to coke in the elevated temperature portions of the reactor loop upstream of the reactor, such as the feed side of the hotter feed/effluent exchangers and the reactor feed/charge furnace.

These risk factors can conspire to produce truly horrific outcomes. For example, seven workers were killed at the Anacortes, Washington (U.S.) refinery in 2010 when an NHT feed/effluent exchanger shell constructed of non-post-weld heat treated (non-PWHT) carbon steel catastrophically ruptured due to HTHA near the welds when putting an exchanger bank into service after cleaning near the cold-end of the exchanger. The shell side saw mixed oil and gas feed; effluent was on the tube side.[1]

Feed/effluent exchanger metallurgy. FIG. 2 is a simplified example of an NHT feed/effluent exchanger train, with representative process conditions at the hot and cold ends, and typical grassroot or replacement metallurgy selections. The shell and tube sides are not specified, as either side can operate with feed and effluent.

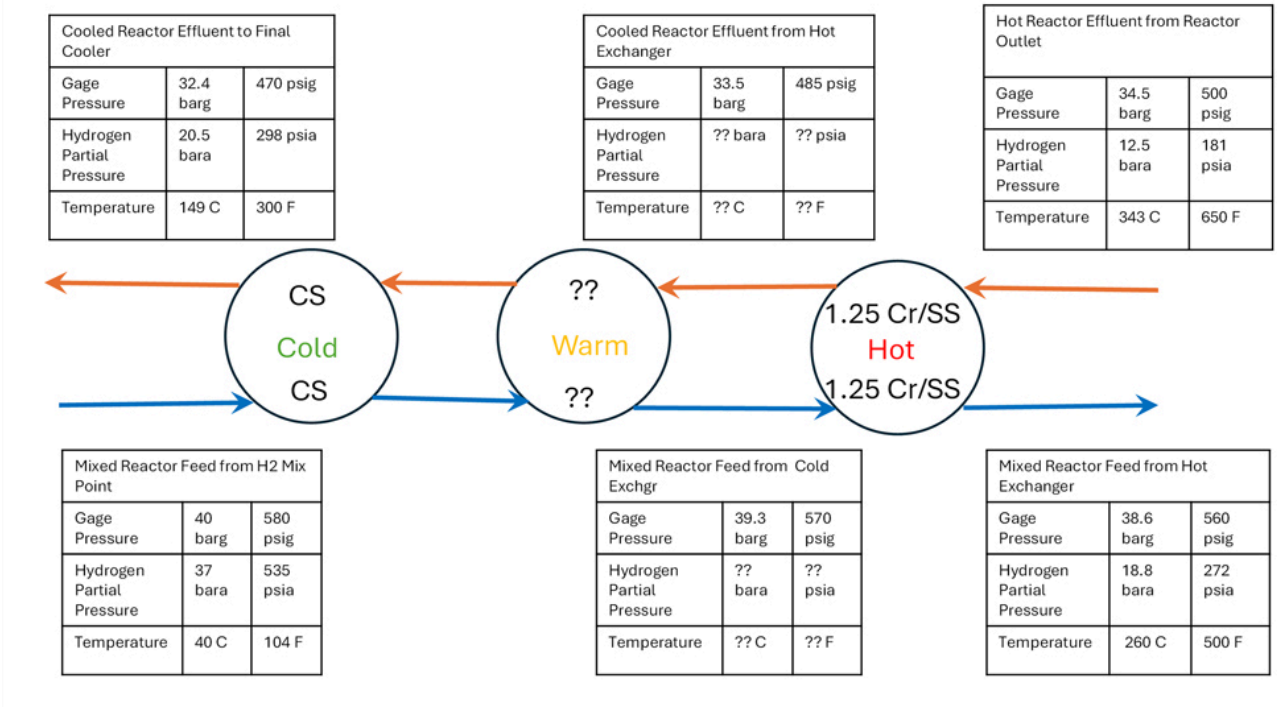


FIG. 2. A simplified NHT feed/effluent heat exchanger train.

Start with mixed feed heating (the blue flows in **FIG. 2**). Since the low-sulfur feed oil enters the NHT relatively cool at approximately 40°C (104°F), carbon steel is the typical metallurgy both upstream and downstream of the H_2 mix point. Even though this is the highest H_2 partial pressure portion of the reactor loop, the temperatures here are low enough that neither HTHA nor high-temperature H_2-H_2S damage mechanisms are a big concern, at least in the coldest exchanger.

Note in **FIGS. 2–4** the large variation in H_2 partial pressure across the train. It changes by a factor of ~2 on both sides of the train from hot to cold. This is driven by the factors discussed earlier: oil vaporization/condensation, oil molecular weight and low gas/oil ratio. Total pressure changes also impact partial pressure and can be amplified by plugging or fouling in the system.

Moving to the hot exchanger, since the mixed feed is now heated, HTHA and high-temperature H_2-H_2S become a concern on both the feed and effluent sides of this service. These would typically drive the metallurgy selection at the hot exchanger to an appropriate combination of 1.25 Chromium-0.5 Molybdemum (1.25 Cr-0.5 Mo) or better, and stainless steel to manage risk.

FIGS. 3 and **4** show a simplified version of the API 941 Nelson curves for both non-PWHT welded carbon steel and welded PWHT carbon steel. These figures illustrate HTHA risk, and how it changes for the reactor feed and effluent sides of the train.

FIG. 3 shows normal operations for reactor effluent cooling. The reactor effluent, at the reactor outlet, is on the upper/right hand (wrong) side of both carbon steel curves, reinforcing the need to select an alloy

with higher resistance to HTHA, such as 1.25 Cr-0.5 Mo. High-temperature H_2-H_2S curves (not shown here) would typically also indicate the need for stainless steel to be present to manage corrosion rates.

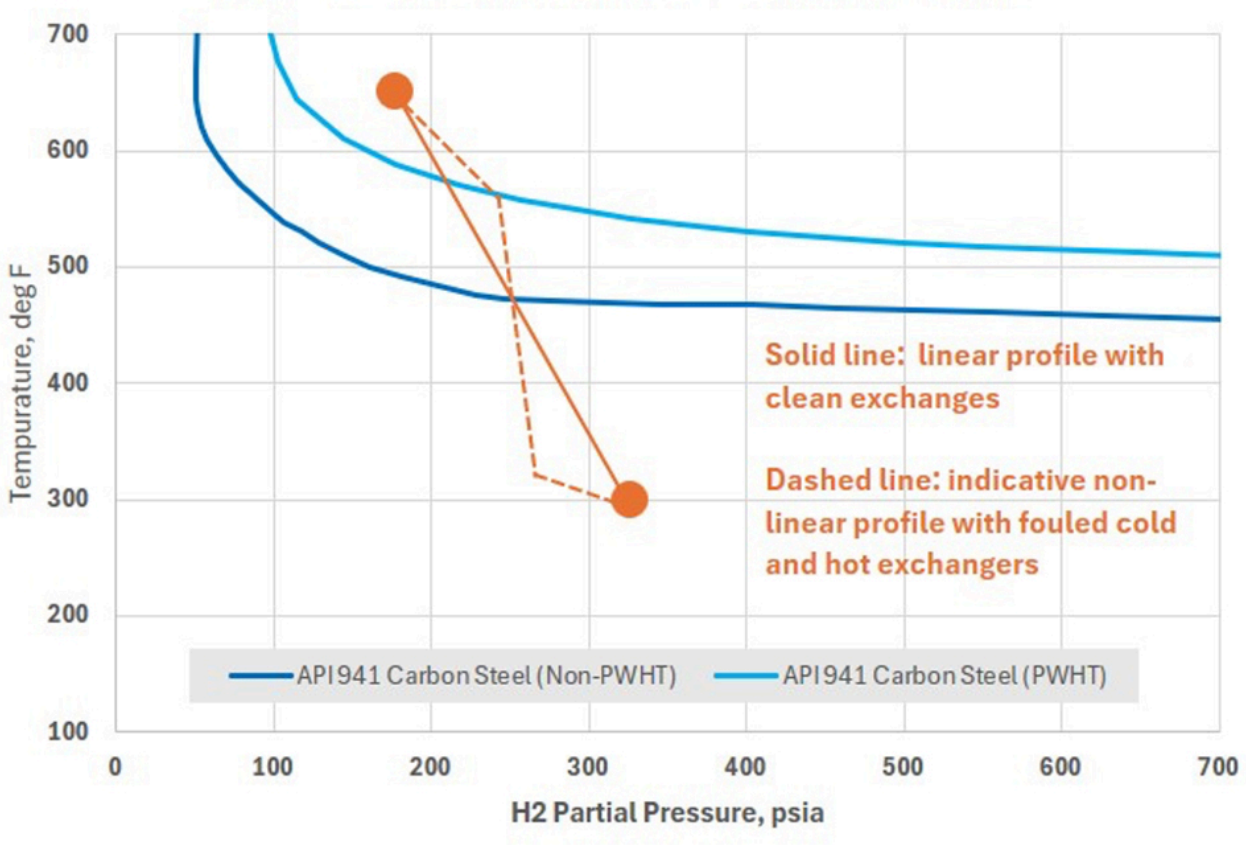


FIG. 3. Reactor effluent cooling HTHA risk.

FIG. 4 depicts the heating path of the feed. It shows the feed that is exiting the hot exchanger is within 10°C (18°F) of the PWHT carbon steel curve. Given that this temperature can be hotter with clean exchangers, and since it is typical to design with a margin to the curves, the metallurgy selection here should strongly resemble the reactor effluent side of the hot exchanger.

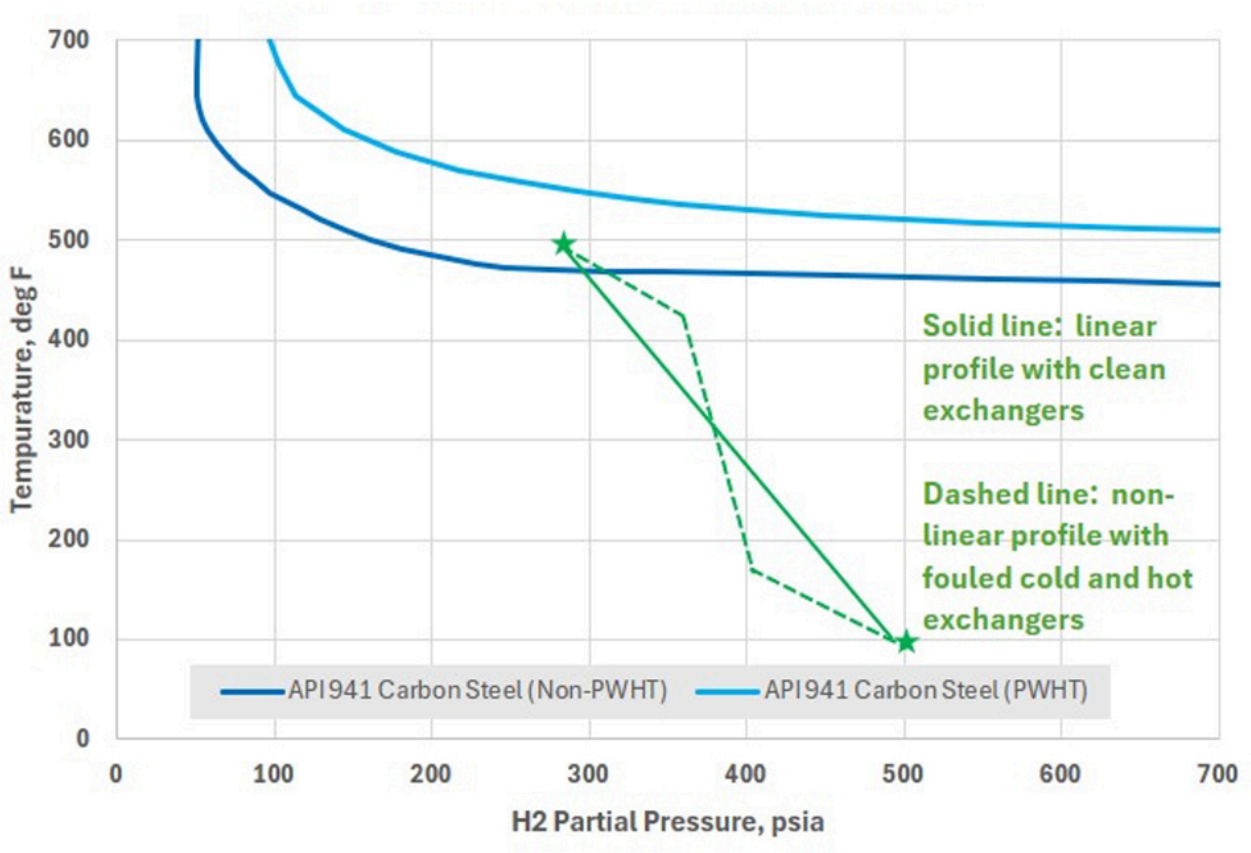


FIG. 4. Reactor feed heating HTHA risk.

On both the effluent and feed sides of this service, the more difficult-to-assess risks occur at the warm intermediate exchanger(s) between the hot and cold—the service that failed in the Anacortes refinery NHT incident. Although the example shows a single warm exchanger, there could be up to four additional exchangers in series between the hot and cold ones. As much as one would like to believe that the temperature profile through these exchangers is linear, it typically is not. Why? NHTs are well known for having two distinctly different fouling mechanisms. These mechanisms can lead to a large variation in the temperatures at the intermediate exchanger vs. what would be expected from a linear profile. A 2015 paper details the two mechanisms: on the feed side, coking at the hotter exchanger(s) due to gum precursors in the feed turning into coke (as discussed earlier); and on the effluent side, chloride and other ammonium halide salt deposition at the cooler exchangers. [2] In trains of three or more shells, there can also be a "Goldilocks" zone in the warm exchanger(s) with little fouling. The combination of these two fouling mechanisms can result in an extremely non-linear temperature profile. The impact of this: the cases studied in literature[2] indicated that the intermediate exchanger effluent/hot inlet could be > 40°C (> 100°F) hotter than what one would assess from assuming a uniform profile, even with the same terminal conditions at both the hot and cold ends of the train. This is why **FIG. 2** shows "??" for the H_2 partial pressures and temperatures at the warm exchanger.

Both the reactor effluent cooling and reactor feed heating curves have dashed lines to denote a non-linear profile path through the intermediate exchanger. In **FIG. 3,** the intermediate operating point on the effluent

side is on the wrong side of the PWHT carbon steel curve with either linear or non-linear fouling. **FIG. 4** is similar, but for the feed side. This non-linear temperature profile—leading to higher-than-expected temperatures in the warm bundle—in addition to the worse-than-expected HTHA resistance of non-PWHT carbon-steel metallurgy (which was not well understood at the time of the Anacortes refinery incident) is why many believe the Anacortes NHT exchanger failed due to HTHA due to sustained operation on the wrong side of the HTHA curve.

Reactor feed/charge preheat furnace and reactor. With few exceptions, the reactor preheat furnace typically operates in a single phase from inlet to outlet, as all oil is vaporized in the feed/effluent exchanger train prior to the furnace inlet. Why? This results from choosing between bad and worse. Would you rather the gum precursors in the feed foul the feed/effluent exchanger, or turn into coke in the furnace? Many would view that coking in the furnace is worse. The furnace tube hot spots, which result from gum precursors and gums in the feed converting to coke as the feed boils out, will not appear in the furnace predictably or uniformly. It would be a matter of atypical good luck to have skin point temperature indications right at the hot spot(s) where the coke deposits. This unpredictable fouling pattern increases the risk that typical furnace hot spot monitoring practices will not catch before a furnace tube leak or rupture results. Compare this undesirable outcome to fouling the hot exchanger(s). Exchanger fouling can be continuously monitored (via pressure drop increase and exchanger feed outlet temperature, among others) and managed to lower severity consequences.

Reactor feed/charge preheat furnace tube metallurgy is typically stainless steel. In some older units, some higher Cr content high alloys are used. Relative to stainless steel, these higher Cr low alloys can generate more corrosion product that ends up in the reactor, increasing the risk of building reactor pressure drop in the run.

As discussed earlier, HTHA and high-temperature H_2-H_2S damage mechanisms govern reactor material selection. For new or replaced reactors, 1.25 Cr-0.5 Mo metallurgy with a stainless weld overlay is a robust selection. That is what industry understands now. Prior to 1990, a curve existed for carbon-0.5 Mo (C-0.5 Mo) in API 941. This curve indicated C-0.5 Mo had better HTHA resistance than carbon steel. The capability of this alloy appeared to be a good fit with the elevated temperature portions of NHTs, and cost less than 1.25 Cr-0.5 Mo, so industry constructed many reactors and feed/effluent exchangers from this base metal. The C-0.5 Mo curve was removed from API 941 in 1990 due to several failures of equipment in Japan, North America and Europe from HTHA operating on the left/below/correct side of the curve. NHTs were not the only process units impacted. Other parts of hydroprocessing and reforming were affected, as well. It is impossible to know how much C-0.5 Mo equipment has been grandfathered into industry and is still in service vs. having been replaced with upgraded metallurgy.

The metallurgy of the NHT mixed-feed heating system can have a dramatic impact on how long the reactor will operate. All the non-stainless-steel alloys in the reactor feed system—including the exchangers,

exchangers to furnace piping, furnace tubes and the furnace to reactor piping—will corrode and generate scale that can come loose and migrate to the reactor. NHT reactors tend to be small relative to feed rate, and the material loaded at the top of the reactor bed will trap the corrosion product from all the upstream equipment. The trapped corrosion product will increase reactor pressure drop and can drive a need to shut down and replace all or part of the reactor bed's contents to correct the process safety/relief overpressure protection and feed rate reductions resulting from the pressure drop build.

Many NHTs have made big improvements to run length by upgrading the furnace tube and furnace-to-reactor transfer line metallurgies to ones with higher high-temperature H_2-H_2S corrosion resistance—e.g., one NHT increased run length without shutdown for NHT pressure drop build from 6 mos to 5 yrs, and another increased runs from 1 yr to 5 yrs by upgrading the furnace to the reactor transfer line to stainless steel. If reducing scale formation by metaling up is not an option, there are also lower cost alternatives to reduce the tendency for reactor pressure drop to build, which will be discussed in Part 2.

Reactor effluent metallurgy: What happens when things get cold and wet? So far, this article has discussed the mechanisms in play for the hot and liquid water-free ends of the plant. Now, the cold end of the plant must be considered, including salts and water. As the reactor effluent cools, the deposition potential for halide salts (typically chloride, but there is also experience with fluoride and bromide) increases. In contrast to most other hydroprocessing units, at the lower NHT operating pressures and gas/oil ratios, the halide salt sublimation point, in normal operations, can occur inside the feed/effluent exchanger train, somewhere in the cooler feed/effluent exchangers. Depending on process conditions (higher chlorides, higher nitrogen, higher pressures, lower gas/oils, etc.), it could also occur at the warmer intermediate exchanger service discussed earlier for high-temperature H_2-H_2S and HTHA risks. So, if there is a need to water wash the warm exchanger(s) to remove the salts, the metallurgy selection becomes even more constrained due to the typical desire to avoid introducing liquid water to stainless steel and minimize the risk of chloride stress corrosion cracking. In contrast to the warm exchanger, the cold feed/effluent exchanger is not as big an issue for wash water injection. As discussed above, it is likely to be carbon steel anyway.

Finally, the unit is ready to finish cooling the reactor effluent to separate oil, water and H_2-rich gas. What drives equipment metallurgy selections here? The final reactor effluent cooler is typically an air cooler but could also be water exchangers. At the typical nitrogen levels and sulfur levels in the feed, the predicted ammonium bisulfide $(NH_4)HS$ content of the effluent would usually indicate that carbon-steel base metal is appropriate. However, $(NH_4)HS$ corrosion is not the only damage mechanism of concern here. In fact, it may not be the primary damage mechanism to worry about. As discussed earlier, halides in the feed not tied up as ammonium salts can produce very acidic conditions at the reactor effluent cooler and downstream separator. Very acidic conditions are obviously a bad fit with carbon steel, as extremely rapid corrosion can result—for example, a brand-new carbon-steel reactor effluent air cooler corroded to a loss of containment within 2 wks in a unit that was experiencing excessive chloride in the feed. For NHTs with

continuous wash water use, frequent monitoring of pH in the first cold separator's water can be a vital early indicator of acid attack. **HP**

Part 2 will be featured in the December issue.

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