

# Protecting your hydroprocessing reactor

## Owners and operators respect a hydroprocessing reactor's minimum pressurisation temperature but can fail to understand factors other than the temperature

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When an owner or operator in charge of a hydroprocessing unit is asked what a reactor minimum pressurisation temperature (MPT) is, they may correctly respond that it is the lowest temperature at which a reactor can start pressurising above a predetermined limiting value after it has already seen hydrogen service. Some may even understand that the purpose of respecting the MPT is to protect the reactor against brittle fracture caused by diffused hydrogen. However, far fewer understand MPT implications beyond those two critical points.

Most hydroprocessing reactors are susceptible to failure mechanisms caused by temper embrittlement as well as hydrogen embrittlement. Whether it be concluding turnaround activities or overcoming an upset condition, respecting the MPT is important to ensure reliable and safe operation of the reactor vessel. This article provides insights and understanding around MPT that can impact hydroprocessing reactor integrity along with other equipment in the high pressure loop that is exposed to hydrogen.

Many papers and industry standards have been published that address concerns surrounding MPT. A recent series of articles by Pillot *et al.* focused on the effect of temper embrittlement and hydrogen embrittlement on a material's mechanical properties,<sup>1</sup> along with a methodology to determine MPT for reactors that are already in service.<sup>2</sup> These two articles provide a framework to further examine MPT for a hydroprocessing unit.

### Temper embrittlement

API RP 571 describes temper

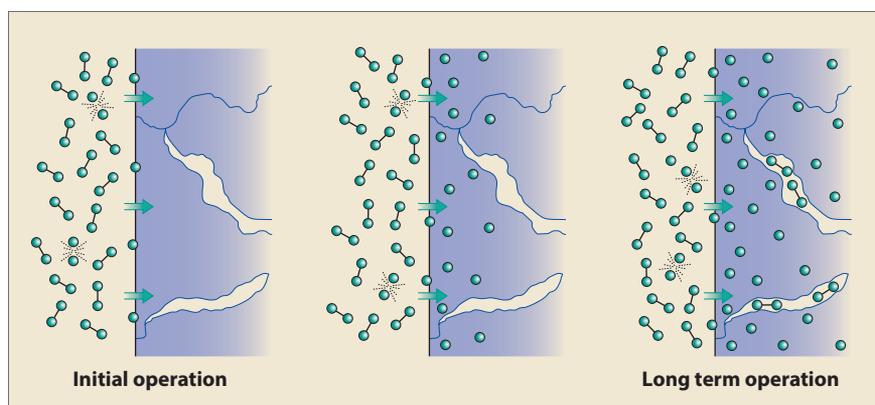


Figure 1 Hydrogen embrittlement

embrittlement as “the reduction in toughness due to a metallurgical change that can occur in some low-alloy steels as a result of long-term exposure in the temperature range of about 650°F to 1070°F (343°C to 577°C). This change causes an upward shift in the ductile-to-brittle transition temperature as measured by Charpy impact testing. Although the loss of toughness is not evident at operating temperature, equipment that is temper embrittled may be susceptible to brittle fracture during start-up and shutdown.”<sup>3</sup>

API 571 best practice recommends limiting the amount of tramp elements such as manganese, silicon, phosphorus, tin, antimony, and arsenic in the base metal and welding consumables to avoid the effects of temper embrittlement. When the steel contains vanadium in the base material, it is less sensitive to temper embrittlement than when the steel does not contain vanadium.<sup>1</sup> It has become standard practice in recent years to use a low alloy steel that contains vanadium with tight control on the tramp elements to fabricate the steel walls of hydroprocessing reactors.

### Hydrogen embrittlement

The National Association of Corrosion Engineers (NACE) describes hydrogen embrittlement as “the ingress of hydrogen into a component, an event that can seriously reduce the ductility and load-bearing capacity, cause cracking and catastrophic brittle failures at stresses below the yield stress of susceptible materials.”<sup>4</sup>

At elevated temperature and pressure, molecular hydrogen partially dissociates to form atomic hydrogen,  $H_2 \leftrightarrow 2H$ , which is a reversible, equilibrium-limited reaction. Atomic hydrogen is soluble in steel and will enter the lattice structure of the walls. The inner surface of the steel becomes saturated and atomic hydrogen starts diffusing towards the outer surface. If a discontinuity or defect is present, then atomic hydrogen that is diffusing through the steel can reversibly form molecular hydrogen in the void, which becomes trapped and starts to accumulate. These trapped pockets of hydrogen create fissures that lead to intergranular cracking. **Figure 1** depicts atomic hydrogen entering the wall and accumulating in the grain boundaries, weakening

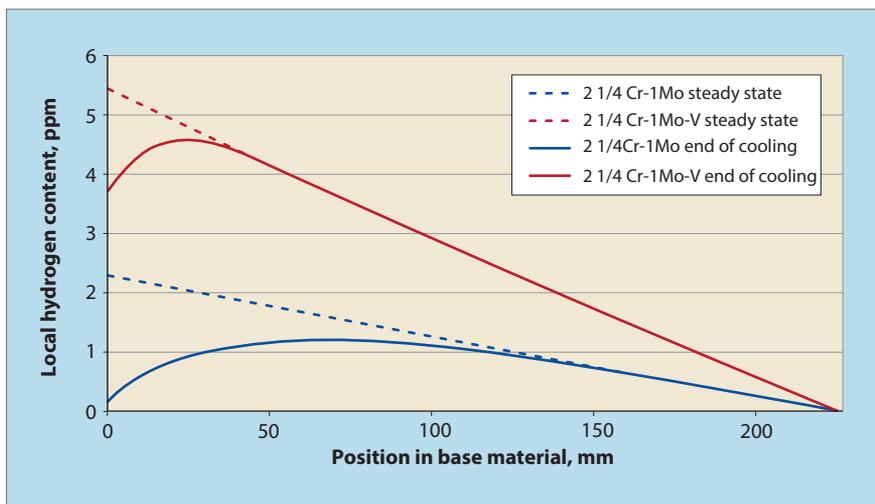


Figure 2 Profiles of H<sub>2</sub> content before and after cooling<sup>1</sup>

the material and leading to a loss of ductility and strength. A reactor wall that has become compromised is not immediately obvious without the assistance of tests and scans. Eventually, microfractures become large cracks that can lead to complete loss of integrity and failure.

As stated previously, MPT is a minimum temperature that must be obtained during start-up before a reactor can be pressurised beyond 25% of its design pressure. Per API RP 571, this 25% point is critical to prevent brittle fracture. The MPT tries to re-establish the equilibrium profile for atomic hydrogen through the steel to minimise the potential for molecular hydrogen being present at the grain boundaries that could result in rapid brittle failure. During unit start-up, this is normally accomplished by heating up a recycle gas stream that passes through the heat transfer coil of a heater before entering the reactor. Once the minimum temperature has been achieved, it is safe to start increasing pressure in the system up to the normal operating point.

Factors such as climate, heater, and compressor size in the hydroprocessing unit will also play an important role in determining the time required to heat up the reactor. It is far quicker to heat up the steel walls of a reactor in a warm climate during the summer months than it is to achieve the same MPT in a cold climate during the winter months.

### Determining MPT

With an understanding of the

mechanisms that lead to brittle failure in a hydroprocessing reactor, how is MPT determined? MPT is a function of fracture mechanics and/or Charpy V-Notch (CVN) toughness calculations. It will not be surprising then that the MPT is normally calculated by the reactor fabricator based on the base material selected for the reactor wall. Common base materials for hydroprocessing reactors include 2 1/4 Cr-1 Mo and 2 1/4 Cr-1 Mo-V. The addition of vanadium allows a reactor of the same size to be lighter in weight. Another advantage with the addition of vanadium to the base metal is the difference in atomic hydrogen content during normal operation. Figure 2 shows an example profile of the hydrogen content through the steel wall between the hot and cold con-

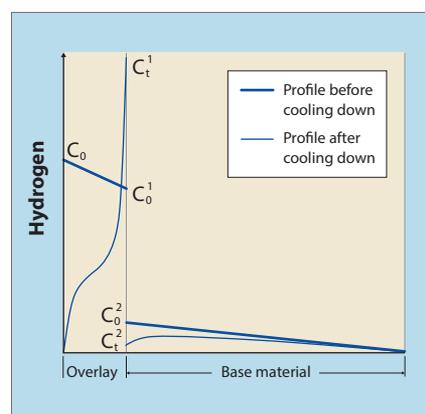


Figure 3 Profiles of hydrogen concentration in material and overlay before and after cooling down of a reactor in a refining plant<sup>1</sup>

dition. Although hydrogen content is higher in vanadium-enhanced steel, the more important feature is that the difference between the hot and cold condition is small, making this a desirable material of construction to use. (There is much less hydrogen diffusing in and out of the wall during a cooldown and heat-up cycle when vanadium is present in the steel.)

Additionally, the base material is usually followed by a stainless steel weld overlay such as 347, which protects the low alloy steel from corrosion and degradation. The addition of this overlay, though necessary, increases the potential for premature failure of the reactor due to a phenomenon known as hydrogen induced disbonding (HID), which is characterised by a crack propagating at the interface between the base material and the austenitic stainless steel weld overlay/cladding.<sup>5</sup> The difference in hydrogen solubility between the base material and the austenitic stainless steel overlay creates a region where hydrogen content goes through a step change (see Figure 3). During reactor cooldown, the interface becomes a point where hydrogen content increases, which will accumulate if a defect is present. Coudreuse *et al.* provide more guidance that identifies how parameters such as operating temperature, hydrogen partial pressure, cooldown rate, material thickness, hydrogen diffusion coefficient and time can influence hydrogen content at the interface.<sup>5</sup> Anecdotal evidence from an API survey suggests that nearly 30% of reactors suffered from HID. ASTM G146 - 01(2018) is the latest industry standard that evaluates disbonding in high temperature, high pressure hydrogen service.

Fabricators can either roll and weld plates or combine forged rings to create reactor shells. Due to the variability in quality and method of supplied base material, it is recommended to work with a list of approved reactor vendors if one is available. These vendors work with experienced suppliers that are more likely to have uniform quality in the base material and thus are less sus-

ceptible to embrittlement. They will also have competency and experience in welding and post-weld heat treatment (PWHT) techniques.

To save time, fabricators may be tempted to re-use exact reactor specifications for a 'copy job', especially if one reactor is already in service and has experienced no issues to date. Reputable fabricators will always confirm the base and filler materials received are specific to a particular project.

### Calculating the MPT

The following example will outline the steps required to analyse a reactor to determine the appropriate MPT. A hydroprocessing reactor with a 300 mm thick wall (base material) that is made of 2¼ Cr-1 Mo with a normal operating temperature of 400°C and pressure of 150 kg/cm<sup>2</sup>g will be examined.

The first calculation step is to determine the susceptibility of the base metal and weld metal to temper embrittlement through calculation of the fracture appearance transition temperature (FATT). The FATT at a 99% confidence level is given by:<sup>1</sup>

$$FATT_{99\%} = -15.416 + 0.72670 J_{TE} - 8.0043 \times 10^{-4} J_{TE}^2$$

$J_{TE}$  (Watanabe factor) is a parameter representative of the base metal composition and the maximum recommended value is 100 for 2¼ Cr-1 Mo (per API RP 571). As established earlier, temper embrittlement is a function of the tramp elements in the base metal so it is not surprising that  $J_{TE}$  is a function of the manganese (Mn), phosphorus (P), silicon (Si), and tin (Sn) compositions in the base metal, expressed in wt%.

$$J_{TE} = (Si + Mn) \times (P + Sn) \times 10^4$$

Assuming a  $J_{TE}$  of 100 and solving for  $FATT_{99\%}$  gives a value of 49.2°C. Rounding to the next largest integer, we get a value of 50°C.

The Bruscato factor, denoted X, is a parameter that represents the weld material and the accepted upper limit for 2¼ Cr-1 Mo is 15 (API RP 571). Similar to  $J_{TE}$ , X is a function of phosphorus, antimony,

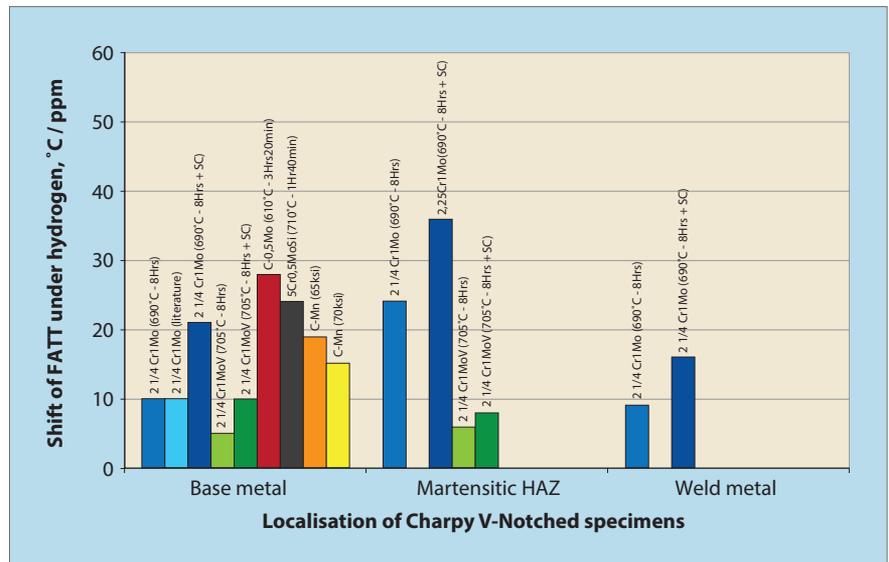


Figure 4 CVN transition curve shift as a function of H content (wtppm) in Cr-Mo(-V) and C-Mn steels<sup>1</sup>

tin, and arsenic content in the weld metal expressed in ppm.

$$X = (10P + 5Sb + 4Sn + As)/100$$

Both  $J_{TE}$  and X are parameters that are controlled by the reactor fabricator during manufacture of the reactor.

Upon shutdown of the reactor, residual hydrogen is present and will therefore impact the integrity of the reactor wall. This requires a correction to be added to the  $FATT_{99\%}$  to account for hydrogen embrittlement. Correlations have been developed to estimate the expected residual hydrogen content in ppm based on operating conditions.<sup>6</sup> The corresponding residual hydro-

gen content at 400°C and 150 kg/cm<sup>2</sup>g for a 300 mm thick wall is 2.1 ppm. Figure 4 shows different values for the shift in FATT due to the presence of hydrogen in units of °C per ppm of hydrogen content in the steel wall.

The industry accepted temperature shift for 2¼ Cr-1 Mo is 10°C per ppm of hydrogen content in the steel. Based on this value, the overall temperature shift is calculated as:

$$\Delta T = (\text{residual } H_2 \text{ content, ppm}) \times (FATT_{99\%} \text{ shift, } ^\circ\text{C/ppm})$$

For the current example,  $\Delta T = 2.1 \text{ ppm} \times 10^\circ\text{C/ppm} = 21^\circ\text{C}$ . The final calculation for MPT is the sum-

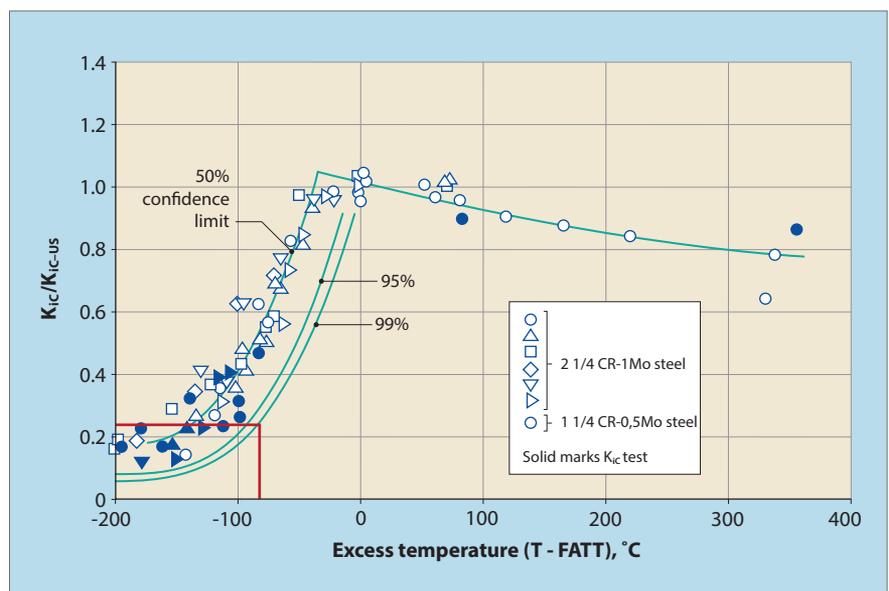
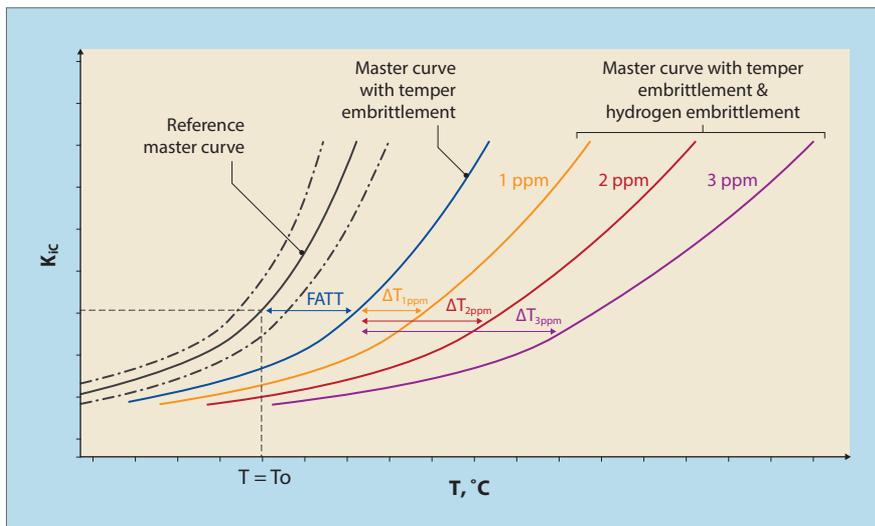


Figure 5 Relationship between  $K_{IC}/K_{IC-US}$  and excess temperature for ferritic steels<sup>7</sup>



**Figure 6** Cumulative effect of ageing and hydrogen embrittlement on quasistatic fracture toughness

mation of  $FATT_{99\%}$  and  $\Delta T$  which is  $71^{\circ}\text{C}$ .

### Calculating the 25% pressurisation temperature

In the next calculation, the minimum temperature necessary to safely pressure up the reactor to 25% of design pressure will be determined. This sets the lower boundary for reactor start-up, even before 25% of design pressure is achieved.  $K_{IC}$  is a measure of the plane strain fracture toughness of a given material. ‘Master Curves’ of these  $K_{IC}$  values can easily be found in the literature for base materials such as  $2\frac{1}{4}$  Cr-1 Mo. **Figure 5** plots the  $K_{IC}/K_{IC-US}$  (‘upper shelf’) ratio against an excess temperature, which is defined as the temperature under consideration minus the  $FATT$ .<sup>5</sup>

In the current example, the  $FATT$  in consideration includes the hydrogen shift (that is,  $MPT$ ). 25% of the design pressure is to be evaluated so the y-axis value of 0.25 for  $K_{IC}/K_{IC-US}$  becomes the starting point. Moving across to the right until the 99% confidence limit is reached and then reading down in **Figure 5** yields an excess temperature of  $-80^{\circ}\text{C}$ . Subtracting  $80^{\circ}\text{C}$  from the  $MPT$  yields a minimum 25% pressurisation temperature of  $-9^{\circ}\text{C}$ . Some fabricators have been known to conservatively round this temperature to  $0^{\circ}\text{C}$ .

Climate was identified earlier as an important factor when consid-

ering start-up time and  $MPT$ . For the current example, a fair weather locale in the middle of summer (southern USA for instance) would have no trouble reaching  $0^{\circ}\text{C}$  for the 25% pressurisation temperature, but it could prove difficult to achieve this temperature in a frigid climate during the middle of winter (say in northern Canada or Russia).

### Older reactors and ageing

Pillot *et al.* correctly point out that the age of a reactor can have a large impact on effective  $MPT$ .<sup>2</sup> As a reactor experiences multiple start-ups and shutdowns, the  $MPT$  will start to increase, possibly requiring longer start-up times. Oftentimes, a refiner will apply a healthy margin above the  $MPT$  so that every start-up will have a consistent temperature to overcome in order to compensate for such ageing. Unfortunately, many older reactors made of CS may also be dealing with the effects of high temperature hydrogen attack (HTHA) as their curves fall well below those for low alloy on the Nelson Curves (API RP 941). **Figure 6** depicts the toughness curves and shifting  $MPT$  of an ageing reactor where the black master curve represents a virgin reactor and the curves to the right represent the effects of temper embrittlement and increasing residual hydrogen.

If initial  $MPT$  is not known, it is possible to remove a test coupon from the reactor (if installed) and

subject it to de-embrittlement heat treatment. Pillot *et al.* noted that reactors built before 1975 with electro-slag welds (ESW) have  $FATT$  values as high as  $170^{\circ}\text{C}$ .<sup>2</sup>

### Start-up challenges

A Russian refiner started up its unit during a time when the ambient temperature was  $-10^{\circ}\text{C}$ . It took some time for the unit to reach  $0^{\circ}\text{C}$  let alone the  $MPT$ . After a couple of days, the reactor finally reached  $MPT$  but there was a problem. Downstream of the reactor was a hot high pressure separator (HHPS) made of the same material as the reactor, which is typical in some hydroprocessing units. This HHPS will have its own  $MPT$  but was having trouble warming up. An inspection of the unit determined that a drain from the HHPS liquid line had been removed during ‘value engineering’. The original purpose of this drain was to allow warm start-up gas to circulate throughout the HHPS and then exit through the liquid outlet line. Without the drain, warm start-up gas simply entered the HHPS and exited through the vapour outlet, completely bypassing the lower half of the vessel. The client ended up using an electric jacket to assist in the HHPS warm-up but this could have easily been avoided had the drain been present.

Ask an operator what the reactor  $MPT$  is and you may get a prompt response. Ask them what their HHPS  $MPT$  is and they will need to search their records for the information. The operating conditions in the HHPS are similar to the conditions in the reactor and as a result the base material of the HHPS is usually the same as the reactor. The HHPS vessel also falls under ASME Sec. VIII Div. 2 of the pressure vessel code. Since it is located in the same high pressure loop, the HHPS is exposed to hydrogen partial pressures that are similar to the reactor. With the same material and comparable residual hydrogen content, one can conclude the HHPS vessel is also susceptible to the effects of temper embrittlement and hydrogen embrittlement like the reactor. During start-up, the HHPS typically

lags the temperature wave increase that is measured in the reactor. It can be expected that once the reactor reaches MPT, the HHPS most likely has not. For cold climates, it would be extremely tempting to start pressuring up beyond 25% of design pressure once the reactor has reached MPT without waiting for the HHPS MPT. It is better to monitor HHPS skin temperatures as well to ensure integrity of the base material for the entire high pressure circuit.

Another refiner had a naphtha hydrotreater that was undergoing start-up. The feed to a naphtha hydrotreater does not require a large amount of heat input to reach reactor operating temperature so instead of using a fired heater, a steam heater was installed. Temperatures were ramped up at a steady rate and the reactor eventually reached MPT. After a few minutes of pressuring up beyond 25% of design pressure, reactor skin temperatures started to drop. When the question was asked about why skin temperatures were dropping, the refiner mentioned they were experiencing some hammering in the utility line and the steam supply to the heater had to be isolated. Understanding the relationship between MPT and pressurisation temperature, the refiner was warned that unless they started depressurising, temperatures would drop below MPT which could lead to serious reactor damage. Once the refiner's engineers heard "MPT" they understood the danger and immediately initiated a depressurisation of the unit. This naphtha hydrotreater was an older unit located in a cold region and its MPT was well above 75°C. In comparison, modern reactors will have MPTs that fall in the range 40-70°C, especially those that conform to API RP 934-A. This example shows how important MPT is not only with increasing temperature but also when temperatures start dropping and the reactor is already above 25% of design pressure.

### MPT as a design consideration

A unit that desires a quick start-up, especially in a cold locale, does

not need to be at the mercy of the MPT. A typical dewaxing unit may have sized the reactor fired heater and recycle gas compressor appropriately for the process but could make start-up of the unit challenging. Adequate over-design in the fired heater should be available not just for the process but also for start-up considerations. Promoting more heat circulation by running a recycle gas compressor and its standby is a strategy that is commonly used. If the compressor does not have an installed standby, it is possible to use a temporary boost compressor solely for start-up pur-

## The process engineer/operator should always consider MPT not only when starting up but also when temperatures start to fall, whether it is on purpose as in a shutdown or otherwise

poses. As illustrated by the example above, adding a drain valve to the HHPS liquid line should also promote even heating of the vessel and ensure the MPT is met here also.

### Conclusion

The process engineer/operator should always consider MPT not only when starting up but also when temperatures start to fall, whether it is on purpose as in a shutdown or otherwise. There may be another vessel in the high pressure loop similar to the reactor that also has its own MPT value and that must be considered before any pressurisation above 25% of design pressure is initiated. Not knowing the MPT can result in a catastrophic failure so consult original records or have a coupon from the reactor tested (if available) to determine an appropriate MPT. The attainment

of MPT can be challenging in some locations but there are solutions that can be implemented either during the design phase or even after the unit has been built, to achieve a fast, safe, and reliable start-up of the hydroprocessing unit.

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