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Optimization of Minimum Safe Pressurization Temperature (MSPT) for Hydroprocessing Reactor

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ABSTRACT

Hydroprocessing units use thick wall low alloy steel materials (typically 1.25Cr-0.5Mo, 2.25Cr-1Mo & 2.25Cr-1Mo-V) for the reactor and feed-effluent exchangers. These materials have superior high temperature strength and high temperature hydrogen attack (HTHA) resistance, but are susceptible to other damage mechanisms, such as temper embrittlement and hydrogen embrittlement, which are time dependent, and hence develop over years of exposure to high temperature and high pressure hydrogen environment. This causes a shift in the ductile-to-brittle transition temperature of these materials. In view of the above material degradation phenomena, pressurizing the equipment at low temperatures can result in catastrophic brittle fracture. To prevent this, Minimum Safe Pressurization Temperature (MSPT) is calculated and the equipment can only be pressurized up to 1/3rd of the design stress or 55 MPa (8 ksi), whichever is lower, until this temperature is reached. Normally, MSPT for the reactor is provided by the Process Licensor/Reactor Manufacturer during the design stage or manufacturing stage, and it has been invariably observed that this temperature is specified with lot of conservatism at a higher level. However, this MSPT can be optimized (lowered down) based on material degradation levels, and this change can bring in significant reduction in the startup and shutdown time of the reactor.

Keywords: MSPT, Hydroprocessing Reactor, Temper Embrittlement, Hydrogen Embrittlement

INTRODUCTION

Heavy wall low alloy steel rectors are used in refinery hydroprocessing units such as hydrocracker and hydro-desulphuriser units, and these are designed to operate at high temperatures, high pressures and high hydrogen partial pressures. The primary pressure boundary is fabricated from low-alloy steel (e.g. Chromium-Molybdenum or Chromium-Molybdenum-Vanadium steel). The other component is a thin corrosion resistant layer of austenitic stainless steel. While small components can be fabricated from clad plates, the liner in large and thicker components is typically a weld overlay. The primary function of the low-alloy steel is to provide the strength and toughness necessary for a pressure boundary at high pressures and temperatures. The function of the stainless steel weld overlay is to protect the low-alloy steel from corrosion[1].

Figure 1 gives the evolution of different generations of Cr-Mo steels for hydroprocessing reactors[2].

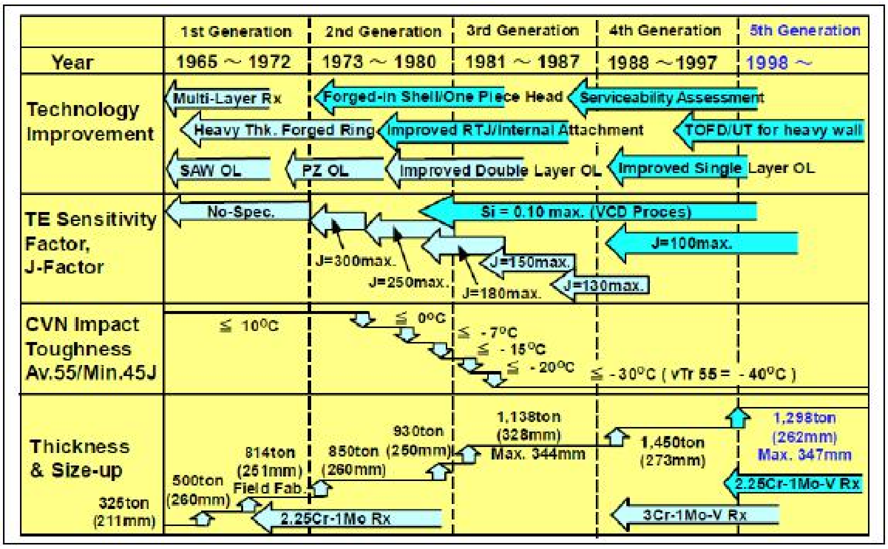

Figure 1: Different generations Cr-Mo steels for reactors and improvement in manufacturing technologies.

Due to the material damage mechanisms associated with low alloy steels and the severe operating conditions, these equipment are susceptible to the risk of catastrophic brittle fracture at lower temperatures. During unit startup and shutdowns, strict attention must be paid to metal temperature and internal pressure to ensure sufficient toughness of the reactor material. This is done by controlling the heating/cooling and pressurization/depressurization rate. In this context, it is very critical to define the Minimum Safe Pressurization Temperature (MSPT) for the reactor and the associated feed-effluent heat exchangers, so that these equipment are not pressurized beyond a threshold level before this temperature is reached during the startup/shutdown cycle.

MSPT for the equipment is estimated based on the following degradation mechanisms, which contribute in reducing the fracture toughness of the low alloy steel material due to exposure to high temperature and high hydrogen partial pressure environment.

(i) Temper embrittlement
(ii) Hydrogen embrittlement

Temper embrittlement of Cr-Mo steels

Temper embrittlement is loss of ductility after prolonged exposure to high temperatures that may be exhibited by specific Cr-Mo steels containing high levels of residual elements. Temper embrittlement occurs after the equipment has operated at elevated temperatures, between 650°F (343°C) and 1000°F (538°C) for long periods of time allowing the impurities to diffuse to grain boundaries. The maximum degree of embrittlement of the steel is directly related to the concentration of these residual elements and the length of exposure to high temperatures. Temper embrittlement can lead to brittle fracture when vessels are pressurized at temperatures well below design in the 100°F (38°C) to 300°F (149°C) temperature range The shift in ductile brittle transition temperature (DBTT) of the material due to temper embrittlement is shown in Figure 2. In the as-fabricated condition, Cr-Mo steel exhibits a low transition temperature typical for steels with good resistance to fast brittle fracture, while after long term elevated temperature service, the steel displays a high transition temperature typical for steels affected by temper embrittlement.

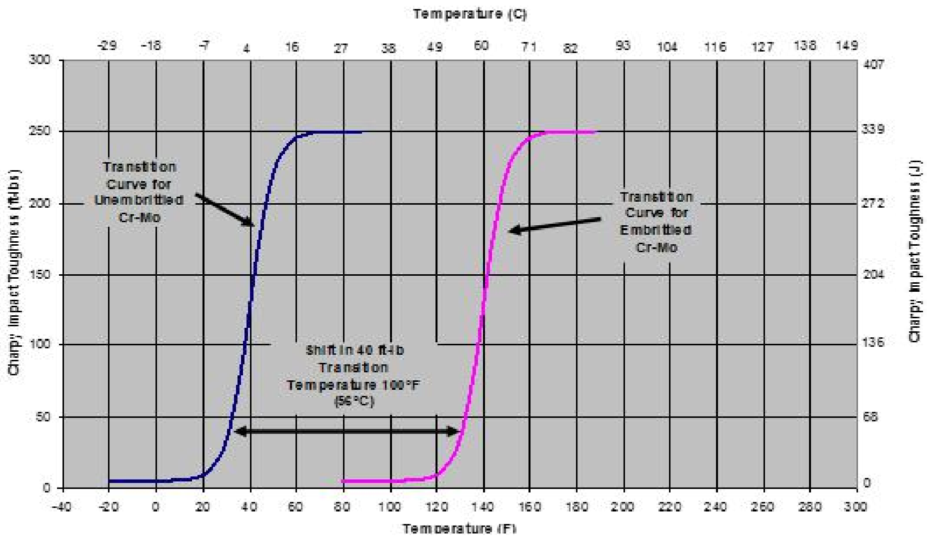

Figure 2: Temper embrittlement is characterized by a shift in the Charpy impact transition temperature[3].

During the fabrication phase, temper embrittlement risks are mitigated by compositional control as required by API RP 934-A [4], as prescribed below.

- For wrought, forged and cast components:

  J-factor = (% Si + % Mn) x (% P + % Sn) x 10^4 (elements in %wt.) < 100

- For welding consumables:

  X-bar = (10 P + 5 Sb + 4 Sn + As)/100 (elements in ppm) < 15

If the above compositional control requirements are followed, a significantly lower MSPT can be achieved as compared to a material with non-controlled composition.

Hydrogen embrittlement

Hydrogen embrittlement is a condition of low ductility in metals resulting from the absorption of atomic hydrogen. Cracking can initiate at an existing defect or location of stress concentration under the combined influence of load and the hydrogen charged condition of the metal.

Similar to temper embrittlement, hydrogen embrittlement reduces low temperature impact toughness of materials and results in an upward shift in ductile brittle transition temperature (DBTT). In the hydroprocessing environment, hydrogen embrittlement is typically the mechanism that governs the MSPT for modern steels, which have a good control over material chemical composition and fabrication aspects.

In this study, the MSPT of a hydro-desulphuriser reactor and the associated feed-effluent heat exchangers in a refinery were assessed in order to optimize the startup and shutdown time.

ASSESSMENT ROCEDURE

The default MSPT recommended by the process licensor was 93°C, which was found to be conservative considering the good steel and fabrication quality used for these equipment. Figure 3 shows the typical equipment layout in a refinery hydrotreater unit and MSPT is applicable for the reactor and the associated feed effluent heat exchangers only since these equipment are made of Cr-Mo steels.

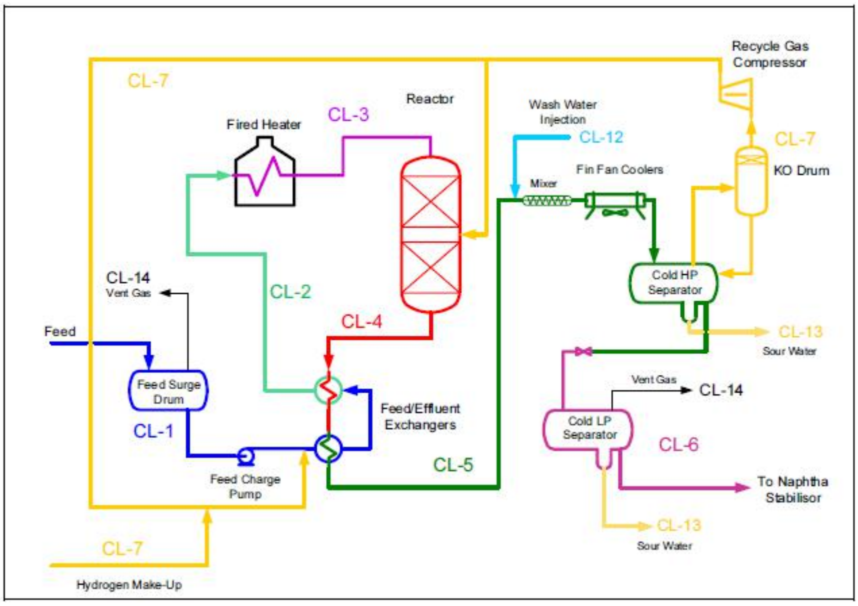

Figure 3: Typical equipment layout in a refinery hydrotreater unit

Following operating conditions were considered for MSPT assessment

- SOR (start of run) conditions : ppH2: 57 Bara at 368 °C

Duration: This condition can be considered for 1 year during 2 year catalyst life.

- EOR (end of run) conditions: ppH2: 50 Bara at 390 °C.

Duration: This condition can be considered for 1 year during 2 year catalyst life.

- HHS (hot hydrogen stripping) conditions: ppH2 : 75.2 bara at 390 °C

Duration: This condition can be considered for 12 hrs per event. Frequency of event can be considered as 2 times per year.

MSPT assessment was done for the worst case considering SOR and EOR operating conditions, i.e., ppH2 57 bara at 390 °C.

Temper embrittlement assessment

Reactor

Material specification:
Shell and heads: 2.25Cr1MoV (SA-542M Type D Class 4a and SA-336M Grade F22V)
Cladding/lining: SS 347 weld overlay
Dimensions:
Internal diameter: 5000 mm, Tangent to tangent height: 20665 mm
Thickness: 105mm (low alloy steel)+4mm (stainless steel)
J factor: 77.09 max.

As per the latest API RP 934-F draft, the recommended MSPT for 2¼Cr-1Mo-V material meeting all step cool requirements included in API RP 934-A and with an end of run temperature of 650°F (343°C) or higher can be set at 24°C. This lower MSPT setting requires that all SAW welds are tested for reheat cracking. During the reassessment, these records were checked and it is confirmed that there was no reheat cracking found during fabrication.

Feed-Effluent Heat Exchangers

Material and fabrication data was analyzed with the following findings:

- Materials used are 2.25Cr1Mo (SA 387 Grade 22, class 2 and SA 336 Grade F22, class 3).
- J-factor < 100 and X-bar < 15 met for all heats of base metals and welds, respectively.
- Impact values at -29 °C checked and all are > 55 J. In some forgings, individual values < 55 J (but > 47 J), but average values > 55 J. This satisfies the requirements of API 934A.
- Step cooling data of weld metal confirms CvTr40 + 2.5 ΔCvTr40 < 10 °C. This is essentially weld material MSPT (CvTr40) during fabrication and an added value corresponding to 2.5 times the transition during step cooling tests (ΔCvTr40), which is considered representative for the shift during the operating life of the equipment.

- Step cooling data for base metal is not available and the tests are not mandated by API 934A.

The above findings confirm that the material and fabrication qualification processes meet the requirements of API 934-A. In line with API 934F draft, the MSPT for temper embrittlement for this material is set at 65 °C.

Hydrogen embrittlement assessment

Two scenarios were identified as the governing scenarios for the reactor and feed-effluent exchangers operation:

- Normal operation: ppH_2 (H_2 partial pressure) of 57 bara at 390 °C (worst case considering start-of-run and end-of-run)

- Hot hydrogen stripping: ppH_2 of 75.2 bara at 390 °C with duration of 12 hrs per event where the event occurs twice a year.

Reactor

For 2.25Cr1Mo-V, HEAC (Hydrogen Embrittlement Assisted Cracking) is the governing failure mode. There are no specific guidelines available to determine its MSPT for hydrogen embrittlement for 2.25Cr1Mo-V. Therefore, a conservative approach was taken by using the available API 934F curves for 2.25Cr1Mo (non V-modified) using a C_{H_Total} of 1.54 at the hot hydrogen stripping conditions. Hot hydrogen stripping conditions were used instead of normal operating conditions because these conditions can increase surface hydrogen levels, especially at nozzle locations or where the weld overlay is not sufficiently thick. The surface hydrogen levels are critical in HEAC mechanism. At these conditions, the dissolved hydrogen in steel is predicted at 3.65 ppm (assuming no weld overlay) using Industeel model.

As per the latest API 934F draft curves, the MSPT is 57 °C for the corresponding dissolved hydrogen in steel for the conservative set of assumptions made above.

Feed-Effluent Heat Exchangers

Hydrogen embrittlement analysis for the feed-effluent exchangers would be the same as the reactor and, in fact, the risk would be significantly lower due to cooling down of the effluent gas and lower thickness of the feed-effluent shell/channel. Therefore, MSPT for hydrogen embrittlement is set at 57°C.

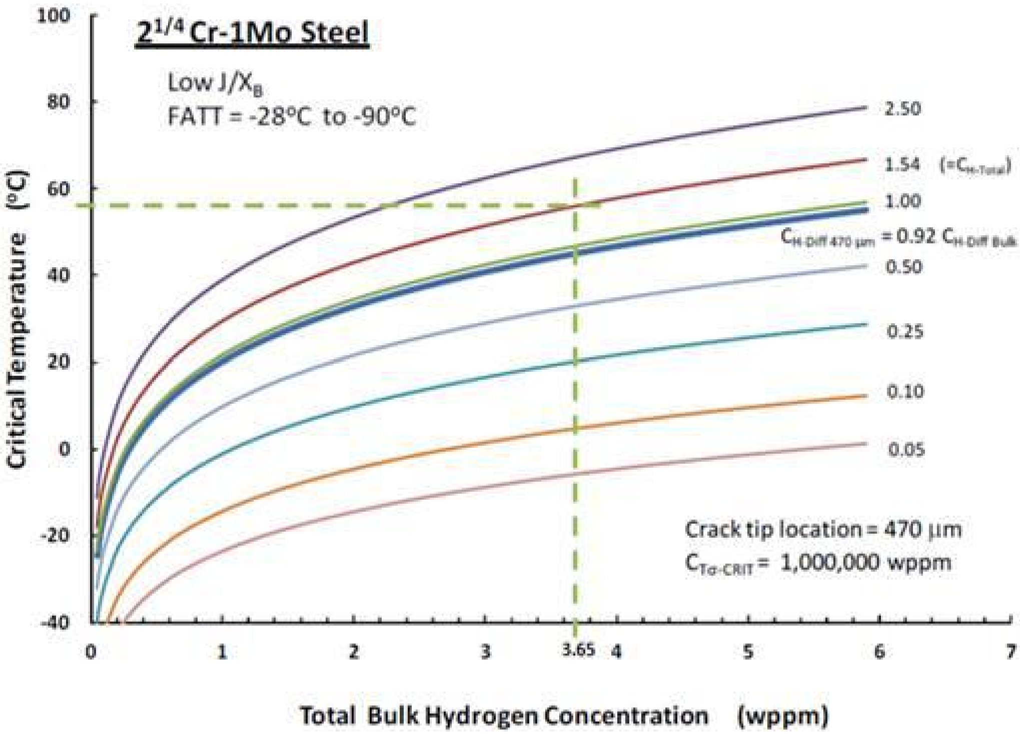

Figure 4: Critical temperature as a function of hydrogen concentration[3]

CONCLUSIONS

MSPT assessed for different mechanisms for the reactor and feed effluent heat exchanger are as follows:

Equipment	**MSPT (°C)**	
	Temper embrittlement	Hydrogen embrittlement
Reactor	24	57
Feed effluent HXs	65	57

The combined MSPT for the reactor and feed effluent exchangers is recommended as 65 °C and is governed by the temper embrittlement of the feed effluent exchanger. This temperature is significantly lower than the earlier MSPT of 93 °C recommended by process licensor. The reduction in 28 °C resulted in saving of 24 hours of star-up/shutdown time.

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