An Overview of Minimum Pressurization Temperature Optimization for Hydroprocessing Reactors

Presented to:
MPC HPV PREVENT Sponsor Meeting
April 16, 2015

Robert G. Brown, P.E.
Phillip E. Prueter, P.E.
Jon D. Dobis, P.E.
Presentation Outline

- Background
  - Hydrocracker Configuration
  - Hydrocracker Design/Construction
- Optimization of MPT Envelope
- Overview of Damage Mechanisms
- How is MPT typically established?
- Updated API 934-F Draft Guidance
- General MPT Assessment method
- Summary
Configuration

Hydrocracker Reactors
Background

- **Typical Design Conditions:**
  - 1100 to 2400 psig $\text{H}_2$ partial pressure
  - 700 to 850°F

- **Typical Materials:**
  - 2-1/4Cr-1Mo N&T (1960s and 70s)
  - 2-1/4Cr-1Mo-1/4V (current choice)
    - R&D of advanced Cr-Mo steel started in 1980s
    - First 2-1/4Cr-1Mo-V reactor was manufactured in 1998
  - Type 308L, 309, 347 SS weld overlay
Optimization of MPT Envelope

- Optimization of heating, cooling & pressurization rates—minimize time, cost and assess relative risk
- Determine validity of the current MPT limitations and establish basis for a recommended MPT for the reactors
- Establish acceptable limits for cool down rates related to applicable failure modes
- Utilize NDE results for cracking directly to establish MPT
- Provide guidance for field measurements to utilize for comparison to the MPT (i.e. what temperature(s) does user monitor as control points relative to MPT)
Optimization of MPT Envelope

- Sample MPT Envelope

![Graph showing the optimization of MPT Envelope. The x-axis represents temperature, and the y-axis represents pressure. The graph is divided into two sections: Unacceptable and Acceptable. Unacceptable is shown from 100% to 60%, and Acceptable is from 60% to 20 to 30%.](image)
Optimization of MPT Envelope

- Optimized Procedure

### Zone #1
Sub-Critical Crack Growth During S/D (Frac. Tough., H₂ ppm, Resid. Stress)

### Zone #2
Hydrogen Embrittlement, Temper Embrittlement and Hydrogen Assisted Cracking (Frac. Tough., H₂ ppm, H₂ PP, Resid. Stress, Operating & Thermal Stress)

### Zone #3
Temper Embrittlement and Hydrogen Assisted Cracking (Frac. Tough., H₂ PP, Resid. Stress, Operating & Thermal Stress)
Optimization of MPT Envelope

- Comparison of Procedures

![Graph showing the comparison between potentially non-conservative and potentially over-conservative conditions based on temperature and pressure. The graph highlights the zone for saving S/D time at approximately 250°F.](image-url)
Damage Mechanisms

- Several damage mechanisms are possible during the start-up/cool-down and shutdown of hydroprocessing reactors
- Brittle Fracture
  - Temper Embrittlement (TE)
  - Hydrogen Embrittlement (HE)
- Subcritical Crack Growth due to hydrogen also known as hydrogen assisted crack growth (HAC)
  - Internal Hydrogen Assisted Cracking (IHAC)
  - Hydrogen Environment Assisted Cracking (HEAC)
- Thermal Fatigue Cracking
- Overlay Disbonding
Damage Mechanisms

Brittle Fracture

- Unstable fracture event
- No apparent plastic deformation before failure
- Requires high stresses, sufficient flaw size, and low material toughness (fracture mechanics triangle)
- Stresses can be residual (welding), thermal, or pressure
Damage Mechanisms

Temper Embrittlement (TE)

- Reduction in toughness due to metallurgical change caused by impurities diffusing to grain boundaries
- Long-term service between 650-1100°F
- TE causes a shift in ductile to brittle transition temperature to higher temperatures (250-350°F for older steels)
- Loss of toughness not evident at operating temperatures; susceptibility to brittle fracture during SU/SD
- Depends on the generation of the steel
  - Function of cleanliness and steel making practices
  - Vessel built prior to 1972 most susceptible; not an issue for modern conventional 2-1/4Cr and 22V (built post 1980)
Damage Mechanisms

Hydrogen Embrittlement (HE)

- Loss in ductility due to effects of atomic hydrogen on grain boundary strength
- Can cause immediate fracture or slow crack growth (HAC) at shutdown
  - Function of the \( H_2 \) ppm level diffused into the steel
- Most pronounced at 70°F and becomes less of an issue above approx. 150°F-180°F
Damage Mechanisms

Through-wall Hydrogen Concentration

Hydrogen Content in Basemetal (Fujii); TSDANAL vs. Benchmark

Hydrogen Concentration (ppm) vs. Distance through-wall (inches)

- Steady state
- End of Cool down
Damage Mechanisms

Diffusivity Comparisons:

![Graph showing diffusivity comparisons for different materials](image-url)
Damage Mechanisms

Solubility Comparisons:

![Solubility Graph](image-url)
Damage Mechanisms

Hydrogen Embrittlement (HE)

Damage Mechanisms

Thermal Fatigue

• Occurs primarily at:
  - Tray rings, chairs, attachments
  - Hydrogen injection mix points
  - Depends on details (newer forged rings/buildups better)

• Function of thermal gradients and cycles
  - If overlay is embrittled more likely
  - If base metal is embrittled, more likely to propagate into the base metal

• Reactors not subjected to significant cycles
Disbonding

- Rarely an issue
- The fusion line has high Cr carbide precipitates and if these are cooled too quickly with a high hydrogen peak at the boundary, may cause cracking between the overlay and base metal
How is MPT Typically Established?

- Production coupons used to determine 40 ft-lb transition temperature from Charpy-V notch transition curve.
- To evaluate TE, a simulated heat treatment called step cooling is required for production coupons.
- A multiplier on the shift of the transition temperature is included and the impact properties should meet the following requirement (current API 934-A):

\[
CvTr40 + 2.5 \Delta CvTr40 \leq 10^\circ C (50^\circ F)
\]

- 40 ft-lb (54J) transition temperature
- Shift in 40 ft-lb (54J) transition temperature due to TE
How is MPT Typically Established?

- The HE of Cr-Mo reactor steels has not been studied as much as TE, as reflected by the limited test data available in the literature.
- The embrittling effect of hydrogen in the steel can be considered as an additional shift of the transition temperatures as follows per Pillot et al.:

\[ CvTr40 + 3.0 \cdot \Delta CvTr40 + C_{H_2} \Delta CvTr40 \leq \text{specified MPT limit} \]

Shift in 40 ft-lb
(54J) transition temperature due to HE (per ppm H2)
API 934 Draft Methodology

- Shift in transition temperature calculated as a function of hydrogen concentration for conventional 2 1/4 Cr.
- Based on dynamic fracture testing conducted by ArcelorMittal on hydrogen charged and uncharged steel
API 934-F Draft Methodology

• Draft developed in 2008 and is in-progress
  - Originally applied specifically to conventional 2-1/4Cr-1Mo
  - H₂ solubility/diffusivity calculations refer to Industeel data (Pillot et. al.) in Appendix C
  - More recent testing has addressed H₂ effects for 22V (Level 1 pressurization temperature = 175°F)

• Methodology
  - Level 1 pressurization temperatures employed as a function of material/impurity levels.
  - Level 2 fast fracture considerations based on API-579 Part 3 Level 2 assessment (essentially UCS-66 of ASME); not based on rigorous fracture mechanics.
    ✷ Slow stable crack growth depends on H₂ concentration (threshold temperature calculation).
    ✷ Level 2 MPT curves not provided for 22V given that HEAC KIH does not vary with temperature; addressed by downtime inspection.
  - More rigorous Level 3 assessments can be performed using FEA.
    ✷ Transient H₂ diffusion analysis can be performed to account for outgassing during shutdown.
API 934 Draft Methodology

• Hydrogen Embrittlement
  - API 934 indicates that H₂ levels need to be well above 3 ppm to promote fast (brittle) fracture
  - High dissolved H₂ concentration not expected after SD, so HE promoting fast fracture does not need to be considered

• Other Research
  - H₂ levels between 2 and 5 ppm actually do affect fracture toughness (Pillot et al. and Sakai et al.)
  - Low to medium H₂ concentration has detrimental effect on toughness
API 934 Draft Methodology

- Typical curve for Rx’s fabricated since 1980 (TE chemistry controls typ.)
- HE is most limiting effect
- Potentially overly conservative for 22V material
API 934 Draft Methodology

- Pre-1980 vessels w/o compositional controls
  - Use a starting temperature of 300°F for developing a Level 1 MPT curve
  - If vessel has electro slag weld (ESW) long seams, use 350°F for developing MPT curve; high impurities in the ESW deposit make them susceptible to TE and 40ft-lb transition temps as high as 300°F have been reported in these welds after high temperature service.

- Post-1980 steels with compositional controls
  - A starting temperature of 200°F should be used for developing a Level 1 MPT curve.
  - Testing of Cr-Mo steels with these compositional controls has shown that the 40 ft-lb (54 J) transition temperature after embrittlement has been well below 150°F (65°C).
  - A starting temperature of 175°F should be used for Level 1 MPT curves for 22V
General MPT Methodology

- Based on Part 9 of API-579 using Failure Assessment Diagram (fracture mechanics basis)
- Stresses: residual and operating
- Assume reference flaw size
  - Coordinate this with NDE results and detectability
  - E.g. 5, 10 and 15 mm crack depths
- Addresses unstable (brittle) fracture and hydrogen assisted crack growth (HAC)
General MPT Methodology

Driving Force

- Simulate temperature response during startup and cool down and tune to measured data; assess sensitivity to changes in heating/cooling rates
General MPT Methodology

Driving Force (Stresses)

- Weld Residual stress from API-579 Annex E or WRS simulation
- Operating pressure and thermal stresses from FEA
General MPT Methodology

Thermal Stress during Cool down

- ID in tension during cool down
- ID in compression during heat-up
- H2 concentration highest on ID
General MPT Methodology

Material Resistance

- Modern conventional 2-1/4Cr
- HAC more limiting than brittle fracture

\[ K_{IH} \text{ and } K_{IC-H} \text{ of Conventional 2.25Cr-1Mo (Wada et. al 2003)} \]
General MPT Methodology

Material Resistance

22V material
- Less affected by HE than conventional 2-1/4Cr
- Susceptibility to brittle fracture is low

$K_{IH}$ of 2.25Cr-1Mo-V (Wada et. al)
22V HEAC Data

- This plot shows that a pressurized hydrogen environment does reduce the stress intensity level for slow stable crack growth in 22V.
- $K_{IH}$ predictions more limiting than IHAC data
- $K_{IH}$ (HEAC and IEAC) for 22V does not depend significantly on temperature

Effect of HEAC on $K_{IH}$ for 22V (API 934F Draft)
General MPT Methodology

Material Resistance

- Currently, limited industry data to adjust toughness as a function of $H_2$ ppm
- MPC $K_{id}$ per API 579 is conservative for assessing brittle fracture in $H_2$ ($K_{IC-H}$)
- Exhibits expected general trend vs. temperature
General MPT Methodology

22V

- Testing performed by the Japan Pressure Vessel Research Council in 2006, by Tanaka et al. indicated that vanadium modified 2.25Cr-1Mo had very low susceptibility to TE and HE.
- More recent work from Pillot et al. also indicated that vanadium enhanced 2.25Cr-1Mo-V steel appeared in every case less susceptible to hydrogen embrittlement than conventional 2.25Cr-1Mo steel.
- Earlier work by Brouwer in 1992 indicates that the hydrogen concentration in the vanadium modified steels are higher during shutdown than in conventional 2.25Cr-1Mo, but the equilibrium pressures related to hydrogen concentration are lower in the vanadium modified steels.
- Therefore, Brouwer indicates that the probability for hydrogen assisted crack growth is strongly reduced in 9Cr-1Mo-V and 3Cr-1Mo-V (22V similar) as compared to conventional 2.25Cr-1Mo.
- Brouwer also indicated that the API 934 recommendations for maximum hydrogen content of 3 ppm is irrelevant for V-modified steels.
Case Study

- **Design Conditions:**
  - 1595 psig at 800°F

- **Material:**
  - Modern 1-1/4Cr (SA-387-11, Class 2); 2003 fabrication
  - PWHT 1275°F

- **Objective:**
  - Cool reactor faster during shutdown
  - Significant economic incentive
Case Study

75 °F/Hr Cooling Rate

Start of N₂ Injection
Case Study

Heat Conducts from Catalyst Bed with Specified Volumetric Heat Flux

- Low Velocity Region (25 BTU/hr-ft²-°F)
- High Velocity Region (800 BTU/hr-ft²-°F)
- Atmospheric (5 BTU/hr-ft²-°F)
- Insulated (0.1 BTU/hr-ft²-°F)
- Temperature Solved or Adiabatic
Case Study

A

Vessel OD Surface

Vessel ID Surface

Vessel OD Surface

Vessel ID Surface

B

S, Max. Principal
(Avg: 75%)

139249
125811
112373
98935
85497
72059
58621
45183
31745
18307
4869
-8570
-22008
Summary

- The draft of API 934-F provides guidance for conventional 2.25Cr-1Mo steels based on a simplified ASME toughness exemption curve approach, and incorporates commentary on recent testing of 22V.
- The current API 934-A requires Charpy V-notch test specimens to determine the 40 ft-lb transition temperature, and includes an adjustment for TE based on step cooled heat treatment tests.
- However, an adjustment for hydrogen embrittlement is not formally addressed, so the MPT cannot be determined directly from material test data.
Summary

- The general methodology presented herein is based on API 579 fracture mechanics methods
  - Allows for optimization of heating, cooling & pressurization rate which can lead to significant reduction in startup/shutdown times—significant cost savings
  - Calculated MPT envelope is integrated with inspection results for cracking—provides guidance for flaw tolerance and inspection planning
  - Rigorous assessment provides insight into equipment structural response and sensitivity to changes in operating conditions