

Inspection, Assessment, and Repair of Heavy Wall Reactor Vessels in High-temperature High-pressure Hydrogen Service

API TECHNICAL REPORT 934-H
FIRST EDITION, MAY 2022



American
Petroleum
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Inspection, Assessment, and Repair of Heavy Wall Reactor Vessels in High-temperature High-pressure Hydrogen Service

1 Scope

This TR documents guidance for the inspection, assessment, and repair of heavy wall reactor vessels (nominally considered a wall thickness of 50 mm (2 in.) and greater) in high-pressure hydrogen service operating at temperatures below 455 °C (850 °F). It provides industry practices dealing with reactor vessels after construction and exposure to operating conditions. It focuses on reactor vessels fabricated from 2¼Cr-1Mo, 3Cr-1Mo, 2¼Cr-1Mo-¼V, and 3Cr-1Mo-¼V steels. It also offers some guidance for heavy wall reactor vessels fabricated from 1Cr-½Mo and 1¼Cr-½Mo steels, but specifically does not pertain to C-½Mo steel vessels. However, guidance included in this document can be used for C-½Mo steel reactor vessels at the owner's discretion and with modifications as appropriate.

This document does not address damage found in hot wall catalytic reforming reactors, fluid catalytic cracking unit (FCCU) reactors, and delayed coking drums as they generally operate at higher temperatures and have thinner walls.

Since this is a technical report, it does not provide recommendations, but instead presents industry experience with case histories of repairs and recognized practices, much of which was documented as part of a Joint Industry Program (JIP) on Aging Reactor Vessels, conducted in two phases between 1995 and 2004.

2 Normative References

There are no normative references in this document.

3 Terms, Definitions, Abbreviations, and Acronyms

3.1 Terms and Definitions

For this report, the following terms and definitions apply in addition to those given in API Recommended Practices 934-A and 934-C.

3.1.1

cladding

Internal integrally bonded corrosion-resistant lining applied as a wrought product to the internal surface of a vessel, i.e. the vessel is constructed from clad plate. Clad plate is fabricated using a hot roll bonding process or an explosive bonding process, and is mostly used for thinner wall reactor vessels. See also lining, overlay, and loose lining.

3.1.2

disbonding

Areas of cladding or overlay that do not have a metallurgical bond to the base metal. Disbonding can occur during fabrication, and testing is typically done to detect and repair any locations. It can also occur due to high-temperature high-pressure hydrogen service depending on the characteristics of the bond areas. Testing of cladding and overlay procedures are done before fabrication to minimize the susceptibility to disbonding.

3.1.3

J-factor

An empirical relationship used to predict temper embrittlement susceptibility of some low alloy steel grade base materials

$$J\text{-factor} = (Si + Mn) \times (P + Sn) \times 10,000$$

where compositional concentrations are expressed in weight percent.

3.1.4

lining

In this document, an internal layer of higher alloy metallic material applied to a less expensive base metal. Forms of lining include cladding, weld overlay, and loose linings.

3.1.5

loose lining

An internal layer of higher alloy metallic material applied to a less expensive base metal by welding thin sheets of the high alloy onto the base metal. This leaves a void under the sheets. Other names for these linings include strip lining and wallpapering. Use of a loose lining typically is not considered acceptable for high-temperature high-pressure hydrogen services.

3.1.6

weld overlay

A form of metallic lining that is applied using a welding process and metallurgically bonded to the base metal. See also cladding, lining, and loose lining.

3.1.7

X-bar

An empirical relationship used to predict temper embrittlement susceptibility of Cr-Mo alloy steel grade weld materials and 1¼Cr-½Mo base metals

$$\text{X-bar factor} = (10 \times P + 5 \times Sb + 4 \times Sn + As)/100$$

where compositional concentrations are expressed in weight parts per million (wppm).

3.2 Abbreviations and Acronyms

AUT	automated ultrasonic testing
CUI	corrosion under insulation
DHT	dehydrogenation heat treatment
FCCU	fluid catalytic cracking unit
FFS	fitness-for-service
FMC	full matrix capture
FMR	field metallographic replication
GTAW	gas tungsten arc welding
HAZ	heat-affected zone
HBW	Brinell hardness with tungsten carbide indenter
HTHA	high-temperature hydrogen attack
ISR	intermediate stress relief
ITP	inspection and test plan
LED	light-emitting diode
LMP	Larson-Miller parameter
MDMT	minimum design metal temperature
MT	magnetic particle testing
NDE	nondestructive examination

PAUT	phased array ultrasonic testing
PQR	procedure qualification record
PT	penetrant testing
PWHT	postweld heat treatment
RCA	root cause analysis
RHC	reheat cracking
RT	radiographic testing
RTJ	ring-type joint
SAW	submerged arc welding
SCC	stress corrosion cracking
SMAW	shielded metal arc welding
SWUT	shear-wave ultrasonic testing
TFM	total focusing method
TOFD	time-of-flight diffraction (a UT technique)
UT	ultrasonic testing
WPS	welding procedure specification

4 Design, Materials, and Fabrication History

4.1 Range of Operating Conditions

The hydroprocessing reactors addressed in this report are fabricated from 2¼Cr-1Mo, 3Cr-1Mo, 2¼Cr-1Mo-¼V, or 3Cr-1Mo-¼V steel alloys. They generally operate at temperatures up to 455 °C (850 °F) with operating pressure up to 20.7 MPag (3000 psig) and with a hydrogen partial pressure up to 90 % of the total pressure. See Section 1 for further discussion of the scope of this document, especially on applying it to heavy wall reactors fabricated from C-½Mo, 1Cr-½Mo, and 1¼Cr-½Mo.

4.2 Material Development History

In the early 1960s, most hydroprocessing reactors were made from annealed 2¼Cr-1Mo steel with a minimum specified tensile strength of 415 MPa (60 ksi). Hydroprocessing advancements then led to the need for greater catalyst volume and larger diameter vessels, which required increased reactor wall thickness. To minimize wall thickness, higher strength quenched and tempered 2¼Cr-1Mo steel was developed for reactor vessels.

The first hydrocracking reactors fabricated from quenched and tempered 2¼Cr-1Mo steel, which had a minimum specified tensile strength of 825 MPa (120 ksi), went on stream in 1966 in the USA. After several months of operation, hydrogen embrittlement cracking was detected in several of these reactors at the same site. Failure investigation of this incident concluded that limiting the tensile strength to ~755 MPa (110 ksi) maximum would prevent hydrogen embrittlement cracking. After this incident, and considering a safety margin, 690 MPa (100 ksi) maximum specified tensile strength became the industry practice for quenched and tempered 2¼Cr-1Mo steel used in heavy wall reactor fabrication.^[1]

In the early 1970s, Japanese fabricators manufactured heavy wall reactors from forged rings that were heated to an austenitizing temperature, quenched in a bath of agitated water, and tempered to the desired strength level. During the same period, formulas limiting the steel impurity levels, namely the J-factor for base metal and the X-bar for weld metal, were proposed as a means of controlling the susceptibility of Cr-Mo steels to temper embrittlement. At that time, steel-making practices would typically produce Cr-Mo steels with a J-factor of up to 300 for plate and forgings and an X-bar of up to 25 for weld deposits. Due to improvements in the steel-making

process during the 1980–1990 timeframe, the J-factor and X-bar are now consistently reduced to less than 100 and 15, respectively.

In the early 1980s, a program was initiated to develop a new grade of 2¼Cr-1Mo steel for reactor vessels, resulting in an enhanced grade with a specified tensile strength range of 585 to 755 MPa (85 to 110 ksi) with a maximum design metal temperature of 455 °C (850 °F). Properties were enhanced by controlling tempering and postweld heat treatment (PWHT) to a narrower temperature range. This enhanced grade of 2¼Cr-1Mo steel was first accepted by the American Society of Mechanical Engineers (ASME) in 1984 in Code Case 1960 and later in 1987 by British Standard BS 5500 in BS Enquiry Case 5500/73. To maintain the enhanced tensile strength of this grade of 2¼Cr-1Mo steel, the minimum PWHT temperature was decreased from 675 °C (1250 °F) to 650 °C (1200 °F). There are some reactor vessels made of thermally enhanced 2¼Cr-1Mo installed in Europe and Asia.

Cr-Mo steel strength levels were further enhanced by adding nominally 0.25 % vanadium. In 1984, ASME Code Case 1961 was approved. This allowed 3Cr-1Mo-¼V-Ti-B steel to be used at metal design temperatures up to 480 °C (900 °F). The first reactors made of 3Cr-1Mo-¼V-Ti-B were installed in Canada in 1990. A similar material, 3Cr-1Mo-¼V-Cb-Ca, was approved as ASME Code Case 2151 in 1993. The first reactors made of 3Cr-1Mo-¼V-Cb-Ca were installed in South America in 1995.

In 1991, ASME Code Case 2098 was approved, permitting 2¼Cr-1Mo-¼V to be used at metal design temperatures up to 480 °C (900 °F) for Division 1 and 454 °C (850 °F) for Division 2. However, up to 1997, the published API Recommended Practice 941 temperature to avoid high-temperature hydrogen attack (HTHA) in the new 2¼Cr-1Mo-¼V alloy was represented by the 2¼Cr-1Mo curve, limiting service temperatures for 2¼Cr-1Mo-¼V to 454 °C (850 °F) maximum. Then, in 1997, a separate curve was added for 2¼Cr-1Mo-¼V, matching the 3Cr-1Mo curve that allowed exposure up to 510 °C (950 °F) at high hydrogen partial pressures. Most refiners apply a 28 °C (50 °F) margin to the Nelson Curve, which results in a 482 °C (900 °F) limit for 2¼Cr-1Mo-¼V. The first reactors made of 2¼Cr-1Mo-¼V were installed in the USA in 1998. Since then, 2¼Cr-1Mo-¼V steel has become the most prevalent material choice for heavy wall hydroprocessing reactors.

4.3 History of Design Stresses from Various Design Codes

Before 1968, ASME *BPVC*, Section VIII (currently ASME *BPVC*, Section VIII, Division 1), ASME *BPVC*, Section III, other national pressure vessel design codes, and design criteria customized by individual companies were used to design hydroprocessing reactors. When using the design rules of ASME *BPVC*, Section VIII, Division 1, the design stress was set at the lesser of 1/4 of the minimum specified tensile strength or 5/8 of the minimum specified yield strength, resulting in a very thick reactor wall. In 1968, ASME published *BPVC*, Section VIII, Division 2, which provides a higher design allowable stress based on the lesser of 1/3 of the minimum specified tensile strength or 2/3 of the minimum specified yield strength. This resulted in a lower design wall thickness for reactor vessels.

In 2007, ASME *BPVC*, Section VIII, Division 2 was rewritten, changing the design stress basis to permit higher allowable stresses based on the lesser of 1/2.4 (42 %) of the minimum specified tensile strength or 2/3 of the minimum specified yield strength. However, the maximum temperature for determining a Division 2 fatigue evaluation was limited to 371 °C (700 °F). In October 2008, Code Case 2605 raised the fatigue evaluation temperature to 454 °C (850 °F) for vanadium modified 2.25Cr materials. In July 2019, Code Case 2605–4 further raised the fatigue evaluation temperature to 482 °C (900 °F). Table 1 shows the increase in the design allowable stress at 454 °C (850 °F) provided by the revision in 2007. (Note that allowable stresses based on time-dependent creep properties added to the allowable stress tables are shown in italics in ASME *BPVC*, Section II, Part D).

Table 1—ASME BPVC, Section VIII, Division 2 Change in Design Stress at 454 °C (850 °F)

Material	2004 Edition, ksi (MPa)	2007 Edition, ksi (MPa)	Increment
Conventional 2¼Cr-1Mo	21.9 (151)	21.9 (151)	0 %
2¼Cr-1Mo-¼V	24.5 (169)	28.9 (199)	18 %
3Cr-1Mo-¼V	23.8 (164)	25.8 (178)	8 %

4.4 API Publications on Reactor Materials and Fabrications

Prior to 2000, heavy wall Cr-Mo reactor vessels had unique requirements concerning material, welding, fabrication, inspection, and examination that were prepared by owners, process licensors, and/or engineering contractors. In 2000, API published API 934 (later superseded by API 934-A), which consolidated basic consensus requirements for fabrication of heavy wall 2¼Cr-1Mo reactors. In the second edition, issued in 2008, the various V-modified versions of Cr-Mo steels were added.

In early 2008, reheat cracking occurred in 2¼Cr-1Mo-¼V submerged arc weld (SAW) deposits during reactor fabrication at several fabricators in Europe.^[2] After several investigative studies, Annex A, entitled *Guidance for Inspection for Transverse Reheat Cracking*, was included to provide nondestructive evaluation (NDE) procedures for detecting transverse reheat cracking. These methods include pulse echo ultrasonic testing (UT) and time-of-flight diffraction (TOFD) UT on shell seams, and phased array UT (PAUT) on nozzle welds. Additionally, Annex-B, entitled *Weld Metal/Flux Screening Test for Reheat Cracking Susceptibility*, provides testing methods for evaluating the sensitivity of SAW welding consumables to reheat cracking.

In 2011, API published API Technical Report 934-B, *Fabrication Considerations for Vanadium-Modified Cr-Mo Steel Heavy Wall Pressure Vessels*, which is a technical report providing explanations, experiences, and knowledge gained from actual problems that have occurred during the fabrication of V-modified Cr-Mo steel heavy wall reactors.

API also addresses the fabrication of 1¼Cr-½Mo and 1Cr-½Mo heavy wall reactor vessels operating at temperatures at or below 441 °C (825 °F) in API Recommended Practice 934-C. This document was originally published in 2008 and contains recommended practices for the fabrication of 1¼Cr-½Mo and 1Cr-½Mo vessels in the quenched and tempered (Q&T) condition in nominal wall thicknesses between 2 in. and 4 in. In 2010, API published API Technical Report 934-D, which is a companion document to API 934-C with explanations and examples involving the fabrication of 1¼Cr-½Mo and 1Cr-½Mo vessels.

API has also published reports on temper embrittlement of Cr-Mo steels. This includes API *Advisory Letter on In-Service Embrittlement of Low-Alloy Cr-Mo Steels*, dated July 30, 1974, and API Publication 959, *Characterization Study of Temper Embrittlement of Chromium-Molybdenum Steels*, issued in 1982.

4.5 Summary of Historical Changes in Reactor Fabrication

Table 2 summarizes historical changes in the design code, materials of construction, applicable API publications, temper embrittlement parameters, low-temperature toughness requirements, and weight and wall thicknesses records for conventional and V-modified Cr-Mo steel hydroprocessing reactors.

Table 2—Historical Changes in Reactor Materials and Fabrication^[3]

Type of Reactor Material and Fabrication	Year																															
	64	66	68	70	72	74	76	78	80	82	84	86	88	90	92	94	96	98	00	02	04	06	08	10	12	14	16					
Reactor Generations ^a	1 st – 1965~1972				2 nd – 1973~1980				3 rd – 1981~1987				4 th – 1988~1997				5 th – 1998~current															
Codes and Standards																																
ASME BPVC, Section VIII Code	Div. 1				Div. 2 (first issued in 1968)				Div. 2 (first issued in 1968)				Div. 2 (first issued in 1968)				Div. 2 (first issued in 1968)				Div. 2 (first issued in 1968)				Div. 2 Rewrite							
Design Stress ^b	Min. S _T 1/4 or S _y 5/8				Min. S _T 1/4 or S _y 5/8				Min. S _T 1/3 or S _y 2/3				Min. S _T 1/3 or S _y 2/3				Min. S _T 1/3 or S _y 2/3				Min. S _T 1/3 or S _y 2/3				Min. S _T 1/2.4 or S _y 2/3							
API 934 milestones ^c																				A			B		C,D	E	F					
Materials for New Fabrication: ^d																																
Q&T 2¼Cr-1Mo and 3Cr-1Mo																																
Thermally Enhanced 2¼Cr-1Mo ^e																																
3Cr-1Mo-¼V-Ti-B ^f																																
3Cr-1Mo-¼V-Cb-Ca ^g																																
2¼Cr-1Mo-¼V ^h																																
Material Properties:																																
J-factor (achievable max. limit)	Not Specified				300				250				180				150				130				100							
Low Temp. Toughness (°C) ⁱ	10				0				-7				-15				-20				-30											
Max. Weight (ton) ^d	500				815				850				1,150				1,450				1,900											
Max. Wall Thickness (mm) ^d	211				297				344				351																			

^a For modern hydroprocessing reactors, as defined by Reference [3] in the Bibliography.^b S_T is tensile strength at design temperature; S_y is yield strength at design temperature.^c A = First edition of API 934 (later renumbered as 934-A), Materials and Fabrication Requirements for 2-¼Cr-1Mo and 3Cr-1Mo Steel Heavy Wall Pressure Vessels (2000); B = Second edition of API 934-A (2008); C = First edition of API 934-A Annex A, Guidance for Inspection for Transverse Reheat Cracking (2010); D = First edition of API 934-B, Fabrication Considerations for Vanadium-Modified Cr-Mo Steel heavy Wall Pressure Vessels (2011); E = First edition of API 934-A Annex B, Weld Metal/Flux Screening Test for Reheat Cracking Susceptibility (2012); F = Third edition of API 934-A, which encompasses Annex A and Annex B (2019).^d Data based on Japanese fabricators experiences.^e Code Case 1960 initially approved in 1984.^f Code Case 1961 initially approved in 1984.^g Code Case 2151 initially approved in 1993.^h Code Case 2098 initially approved in 1991.ⁱ Lowest temperature at which toughness of 55 J (40 ft-lbs) average/45 J (33 ft-lbs) minimum can be consistently achieved.

5 Potential Damage Mechanisms in Heavy Wall Reactor Vessels

5.1 General

There are several in-service damage mechanisms that can affect the properties or condition of Cr-Mo steels used in the fabrication of heavy wall reactor vessels. Each of these mechanisms can lead to cracking and other forms of degradation that can adversely affect the reliability of heavy wall reactor vessels. Additional information on damage mechanisms found in refinery equipment is given in API 571.

5.2 Temper Embrittlement

Temper embrittlement is primarily observed in older reactors. Newer Cr-Mo reactor steels (since the 1990s) have lower concentrations of impurity elements (e.g. S, P, As, and Sn), and, thus, are more resistant to temper embrittlement. It is the result of impurity elements, such as P, Sn, Sb, and As, that diffuse to grain boundaries during elevated temperature service.

Long-term exposure to service temperatures ranging from 345 °C (650 °F) to 595 °C (1100 °F) promotes diffusion of impurity elements to grain boundaries, resulting in a shift of the ductile-to-brittle transition temperature (DBTT) to higher temperatures. Temper embrittlement typically is determined by Charpy V-notch impact testing. Long-term isothermal aging of Cr-Mo steel samples at elevated temperatures indicate that temper embrittlement reaches a maximum level after 20,000 to 30,000 hours of aging at temperature.

Temper embrittlement can promote brittle fracture when the susceptible vessels are pressurized at temperatures below 150 °C (300 °F). Figure 1 shows a typical Charpy impact energy transition curve for a Cr-Mo steel susceptible to temper embrittlement. In the as-fabricated condition, this Cr-Mo steel exhibits a low DBTT temperature typical for steels with good resistance to brittle fracture; however, after long-term elevated temperature service, the steel displays a high transition temperature and increased susceptibility to brittle fracture.

Today's Cr-Mo reactor steels are highly resistant to temper embrittlement with improved compositional controls on both the weld metal and base metal, as well as special testing requirements for the weld metal that demonstrate greatly reduced effects due to temper embrittlement. The J-factor is used to indicate the effect of impurity levels on temper embrittlement in base metals of 2¼Cr-1Mo, 3Cr-1Mo, and the V-modified versions of these steels. The X-bar is used to indicate the effect in all the Cr-Mo weld metals covered by this document and in 1¼Cr-½Mo and 1Cr-½Mo base metal. X-bar is used for 1¼Cr-½Mo and 1Cr-½Mo base metal because they contain intentional additions of Si (nominally 0.50 to 1.00 wt.%), which results in the J-factor not being an accurate indicator of temper embrittlement. See Section 2 for definitions of J-factor and X-bar.

Theoretically, the effects of temper embrittlement can be reversed by a high-temperature heat treatment followed by rapid cooling. A de-embrittling heat treatment involves holding at 600–625 °C (1100–1150 °F) for two hours minimum, followed by water quenching or fast cooling as outlined in API 571 and API Publication 959. However, there are no reported cases where a de-embrittling heat treatment has been performed prior to weld repairs on Cr-Mo equipment affected by temper embrittlement. This is likely to be because it is impractical to achieve the required fast cooling/water quenching from the de-embrittling heat treatment temperature on a reactor without generating large thermal stresses in the area being cooled. As a result, other steps to minimize the risks from embrittlement have been implemented during repairs, such as bake-outs, preheat, and more, as discussed in other sections of this API 934-H document.

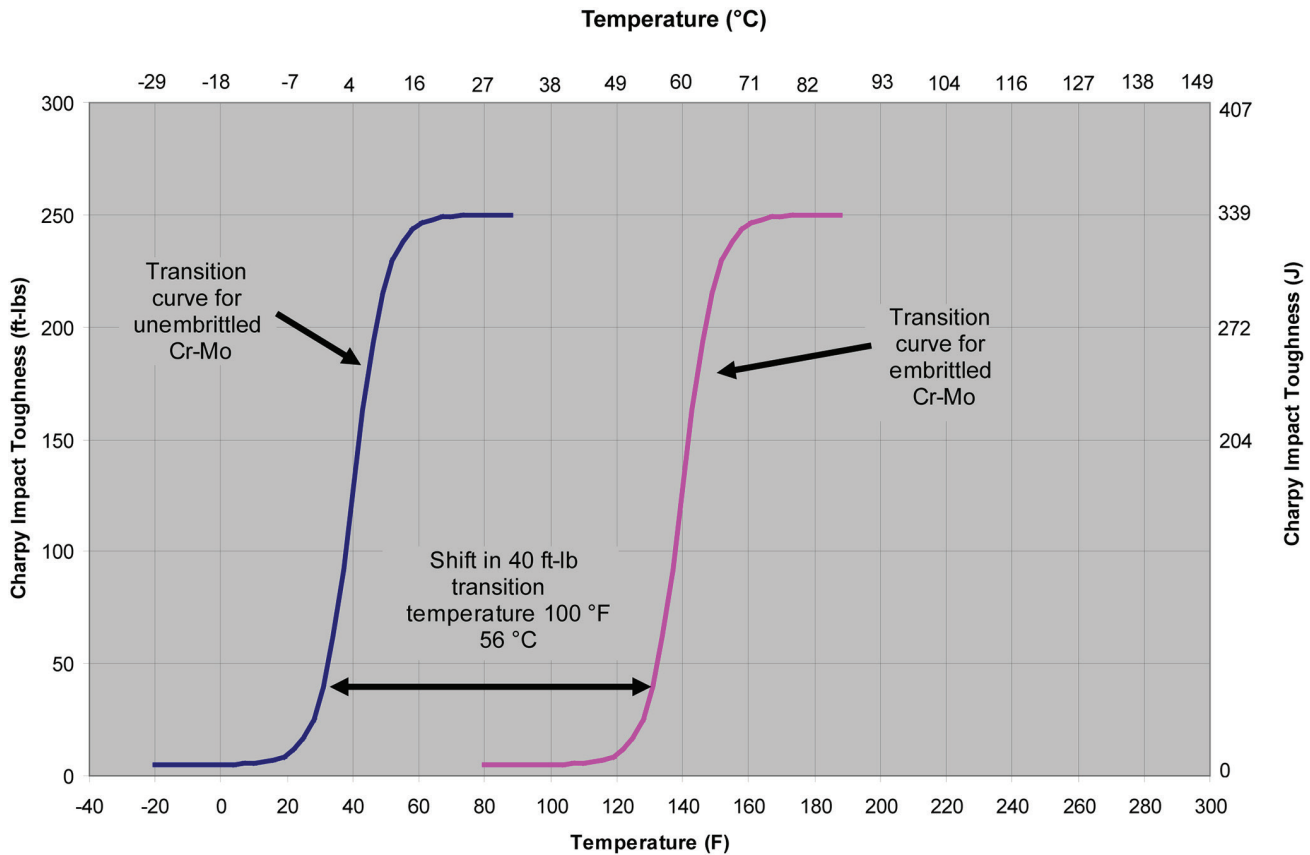


Figure 1—Temper Embrittlement Results in an Upward Shift of the Transition Temperature for Brittle Fracture

5.3 Hydrogen Embrittlement

Hydrogen embrittlement occurs when hydrogen atoms diffuse into susceptible steels. This diffusion occurs while in service at high temperature, and once equilibrium is achieved, the hydrogen concentration in the steel is at the solubility limit. When the reactor is cooled, some of the atomic hydrogen gas diffuses out of the steel. However, the solubility limits vary with temperature, and while the reactor is being cooled for shutdowns, in many cases the hydrogen cannot diffuse out quickly enough and will exceed the solubility limits at lower temperatures. Hence, the hydrogen is trapped in the steel, which can cause temporary embrittlement. The atomic hydrogen that remains in the steel promotes slow stable crack growth at low stress intensity levels—relatively small cracks propagating at low applied stress levels. This form of slow stable crack growth is commonly called hydrogen embrittlement cracking.

Hydrogen embrittlement can occur in Cr-Mo reactor steels at dissolved hydrogen levels normally above 1.5 ppm, at which level hydrogen embrittlement is typically evaluated. Research has shown that slow stable crack growth resulting from hydrogen embrittlement occurs below a threshold temperature that is determined by the hydrogen concentration and impurity levels in the steel. The higher the hydrogen concentration and impurity level in the steel, the higher the threshold temperature for slow stable crack growth. Testing has shown that Cr-Mo steels with a high impurity level and high dissolved hydrogen concentration can have a threshold temperature for crack growth as high as 130 °C (270 °F). These high threshold temperatures for hydrogen embrittlement are based on compact tension (CT) testing conducted at the University of Virginia on hydrogen charged plate samples with a J-factor of 302 and SAW deposit samples with an X-bar of 25.^[7] Recent testing on V-modified 2¼Cr-1Mo steel has shown that it has an enhanced resistance to hydrogen embrittlement, largely due to its high solubility for hydrogen. This enhanced hydrogen solubility has been attributed to the hydrogen trapping sites provided by the presence of vanadium carbides in V-modified 2¼Cr-1Mo steel.^[4–8]

The most common effect of hydrogen embrittlement in heavy wall vessels is cracking and disbonding in the Cr-Mo base metal immediately below SS weld overlay or cladding. Disbonding cracks occur most frequently in

older vessels fabricated from Cr-Mo steel where a weld overlay was deposited using a high heat input welding process such as electroslag welding (ESW). The high heat input welding process generates large grains in the heat-affected zone (HAZ) of the Cr-Mo base metal immediately below the weld overlay. These large grains in the Cr-Mo base metal are particularly susceptible to hydrogen embrittlement and the resulting slow stable crack growth. Experience has shown that disbonding cracks propagate parallel to the surface and do not result in through-wall cracking. API 934-A outlines possible testing (per ASTM G146) of Cr-Mo samples that have been weld overlayed to ensure that disbonding will not occur with the proposed weld overlay procedure. The testing is done at the hydrogen partial pressures and temperatures that simulate similar hydrogen charging as the service conditions. The V-grade steels have proven to be more resistant to disbonding, both by testing and experience, than conventional Cr-Mo grades of steel. Hence, disbonding tests are typically not required for V-grade steels. See API 934-A.

Limited disbonding tests have been conducted on explosively bonded cladding, showing favorable resistance when compared with weld overlay or roll bond applications. Both explosive bonded and hot roll bonded claddings have shown successful experience with no disbondment at typical operating conditions. For each application, testing of the clad materials for disbondment resistance is generally performed per API 934-A or API 934-C when justified based on the operating conditions.^[31, 32]

5.4 Sigma Embrittlement and Cracking of 300 Series Stainless Steel Overlays

Most heavy wall vessels contain a layer of 300 series stainless steel (SS) weld overlay or cladding on the inner diameter (ID) surface to provide resistance to sulfidation corrosion. In thinner wall reactor vessels, hot roll bonded or explosive bonded clad plate is often used to provide the internal lining. However, weld overlay is used on thicker vessels, and the SS weld deposits can experience sigma embrittlement and cracking from exposures to high temperature. In the as-welded condition, the weld overlay will contain a level of delta ferrite (typically between 3 and 10 vol.%) that transforms to sigma phase during PWHT. In addition, this layer of 300 series SS weld overlay is left in residual tension following PWHT of the vessel during fabrication due to the difference in thermal coefficient of expansion between the lining and Cr-Mo base metal, and it then experiences additional cyclic thermal stresses each time the vessel goes through a startup and shutdown cycle. These tensile thermal stresses in the weld overlay are very high and exceed its yield strength level when the reactor is cooled to ambient temperature.^[9] This can result in low cycle fatigue cracking in the weld overlay after multiple startup and shutdown cycles, especially in areas where the thermal stresses can be concentrated, such as at the toes of internal attachment welds. This low cycle thermal fatigue effect is further discussed in 5.9.

In older vessels, SS weld overlays typically display a greater tendency to crack compared with a weld overlay applied today. This is because there were fewer compositional and impurity control requirements for the overlay welding consumables in older vessels, which resulted in high levels of sigma phase and/or other phases that promoted poor ductility in the overlay after the vessel was subjected to PWHT.^[9,10] In the older versions of 300 series SS weld overlay, compositions favored higher delta ferrite levels in the deposit to prevent hot cracking tendencies. This was particularly the case for older versions of Type 347 SS weld overlay, which has a stronger tendency for hot cracking in the weld deposit than other grades of 300 series stainless steel. In general, delta ferrite levels above 8 % can result in significant reductions in fracture ductility due to sigma phase formation during PWHT. This low level of fracture ductility can result in cracking of the weld overlay after a relatively few startup and shutdown cycles.

In addition to an inherently poor resistance to cracking from thermal cycles, laboratory testing summarized in Welding Research Council (WRC) Bulletin 240 has shown that a 300 series SS weld overlay deposit with high levels of sigma phase can also display a reduced ductility due to hydrogen charged into the overlay during service.

Today, the ferrite content and composition of SS weld overlays are controlled to minimize these potential problems. Additionally, in cases where the weld overlay is applied in two layers, the second layer typically is applied after PWHT so that the second layer does not have the delta ferrite in the weld deposit converted to sigma phase.

5.5 Polythionic Acid Stress Corrosion Cracking of SS Items

In general, 300 series SS exposed to temperatures above 370 °C (700 °F) for straight grade Type 304 and Type 316 can become sensitized and susceptible to polythionic acid stress corrosion cracking (PASCC). These straight grades of SS also sensitize during welding. Low carbon grades of 300 series SS are resistant to sensitization from welding and typically do not sensitize in service at temperatures below ~400 °C (750 °F). Chemically stabilized grades of SS such as Types 321 and 347 stainless steels are resistant to sensitization from welding and typically do not sensitize in service at temperatures below ~454 °C (850 °F). The actual temperature above which sensitization will occur depends on the specific grade of 300 series SS and whether it is welded. Sensitization can also occur when some grades of SS are exposed to the PWHT temperatures of low alloy steels, but the low carbon and stabilized grades are generally resistant based on the relatively short times of exposure.

PASCC occurs during downtimes when an iron sulfide scale on the surface of sensitized SS is exposed to water and air. In reactor vessels, the tensile stresses that drive PASCC are usually associated with welding residual stresses or the residual stresses resulting from thermal cycling.

It has been shown that weld overlay linings are very resistant to PASCC.^[11] Reportedly, weld overlay displays a high resistance to sensitization due to the fine dendrite cell size produced in the overlay deposit.^[12] Hence, the primary concerns of PASCC are on SS cladding and internals. As a result, it is important to use grades of 300 series SS for wrought product cladding and internals that have an inherently enhanced resistance to sensitization both during fabrication and service, such as Types 304L, 316L, 321, and 347 stainless steels.

Several owners report that they circulate or spray a soda ash solution in hydroprocessing reactors and sometimes additional components when cooled for shutdowns, as outlined in NACE SP0170, to prevent PASCC. This is reportedly to protect SS internals or cladding (when predicted to be sensitized), or other SS piping, exchangers, etc. As noted in 5.6, remnant water from the circulation of a soda ash solution has caused chloride stress corrosion cracking (SCC) or alkaline (caustic) SCC of 300 series SS components in the unit, such as low point piping drains, shortly after startup. This has resulted in significant unplanned outages. As a result, many owners use other practices during a shutdown, as outlined in NACE SP0170, that do not involve the circulation or spray of a soda ash solution. However, if none of the SS components are predicted to be sensitized, then many owners do not require any of these practices.

5.6 Chloride Stress Corrosion Cracking of SS Items

Chloride SCC can occur in a 300 series SS if exposed to water and chloride ions above ~60 °C (140 °F). As discussed in 5.5, the source of the chloride ion in some reports of chloride SCC in hydroprocessing reactor circuits has been attributed to the soda ash solution used to neutralize the SS surface during downtimes to prevent PASCC. The SCC is believed to have occurred when the soda ash solution was not drained thoroughly, and pockets of solution became trapped in drains, low points, or dead legs. Once the unit is restarted, the soda ash solution heats up, and in some cases, boils at the high operating temperature and pressure. This results in conditions conducive to chloride SCC, even though the water and soda ash contained chloride ion levels that met the limits allowed in NACE SP0170.

Chloride SCC also has been identified as a contributing factor causing ring-type joint (RTJ) flange cracking as discussed in 6.8 and has been observed in SS vertical bed thermowells initiating from the inside surface. The latter has been attributed to rainwater getting into the thermowell during a shutdown. The cracking has typically occurred shortly after startup when the water heats up. Preventing water entry is the primary means of avoiding this cracking. Some older reactors have solid SS catalyst dump nozzles that have also suffered chloride SCC. In newer reactors, these nozzles are Cr-Mo overlayed with SS so that chloride SCC occurring in the overlay does not propagate through the underlying Cr-Mo.

5.7 High-temperature Hydrogen Attack

High-temperature hydrogen attack (HTHA) occurs when dissolved hydrogen reacts with carbides in the steel to form internal methane that promotes fissuring and cracking. The threshold conditions for HTHA of various materials and other information about the HTHA mechanism, detection, etc. are given in API 941. HTHA has not been observed in heavy wall vessels fabricated from Cr-Mo steels because these steels form carbides

that contain adequate alloy to prevent the reaction with hydrogen that forms methane at the hydroprocessing operating conditions. There are a few incidents of HTHA in heavy wall C-1/2Mo reactors reported in API 941.

It is recognized that a 300 series SS cladding or overlay integrally bonded to a heavy wall ferritic steel reactor provides a reduction in the hydrogen content of the base metal during operation, and hence a reduction in the risk of HTHA. Due to the increased hydrogen solubility and reduced hydrogen diffusion rates in 300 series SS, the stainless steel acts as a barrier that essentially reduces the hydrogen partial pressure for the underlying ferritic steel. API 941 contains guidance on how to determine the lowering of hydrogen levels in base metals provided by an integrally bonded 300 series SS cladding or overlay in a heavy wall ferritic steel reactor. Some older vessels and exchangers used loose SS liners in nozzles that were welded at both ends of the cylinder, and these liners do not provide any benefit in reducing the risk of HTHA of the base metal.

5.8 High-temperature Sulfidation

Heavy wall reactor vessels containing high levels of H₂S are lined with a 300 series SS cladding or weld overlay to resist sulfidation corrosion. At maximum expected operating conditions of temperature and H₂S levels, the Couper-Gorman curves in API Recommended Practice 939-C indicate that a corrosion rate of well below 0.05 mm/yr (2 mpy) is expected on stainless steel. However, even at this very low corrosion rate, enough sulfide scale can accumulate in the catalyst bed and on the outlet screens to cause a high pressure drop across the reactor. Several owners have aluminized screens in the reactors to minimize scale formation and the resulting pressure drop.

Some hydrocracking processes have minimal sulfur in the feed and use Cr-Mo reactors with no internal linings. No significant sulfidation has been reported, but these reactors cannot be changed to a service in which the feed contains sulfur. Some reactor vessels were lined with 12Cr SS cladding (such as grades 405 or 410S). These grades display reduced sulfidation resistance compared with 300 series SS cladding, and the corrosion rates can be difficult to monitor.

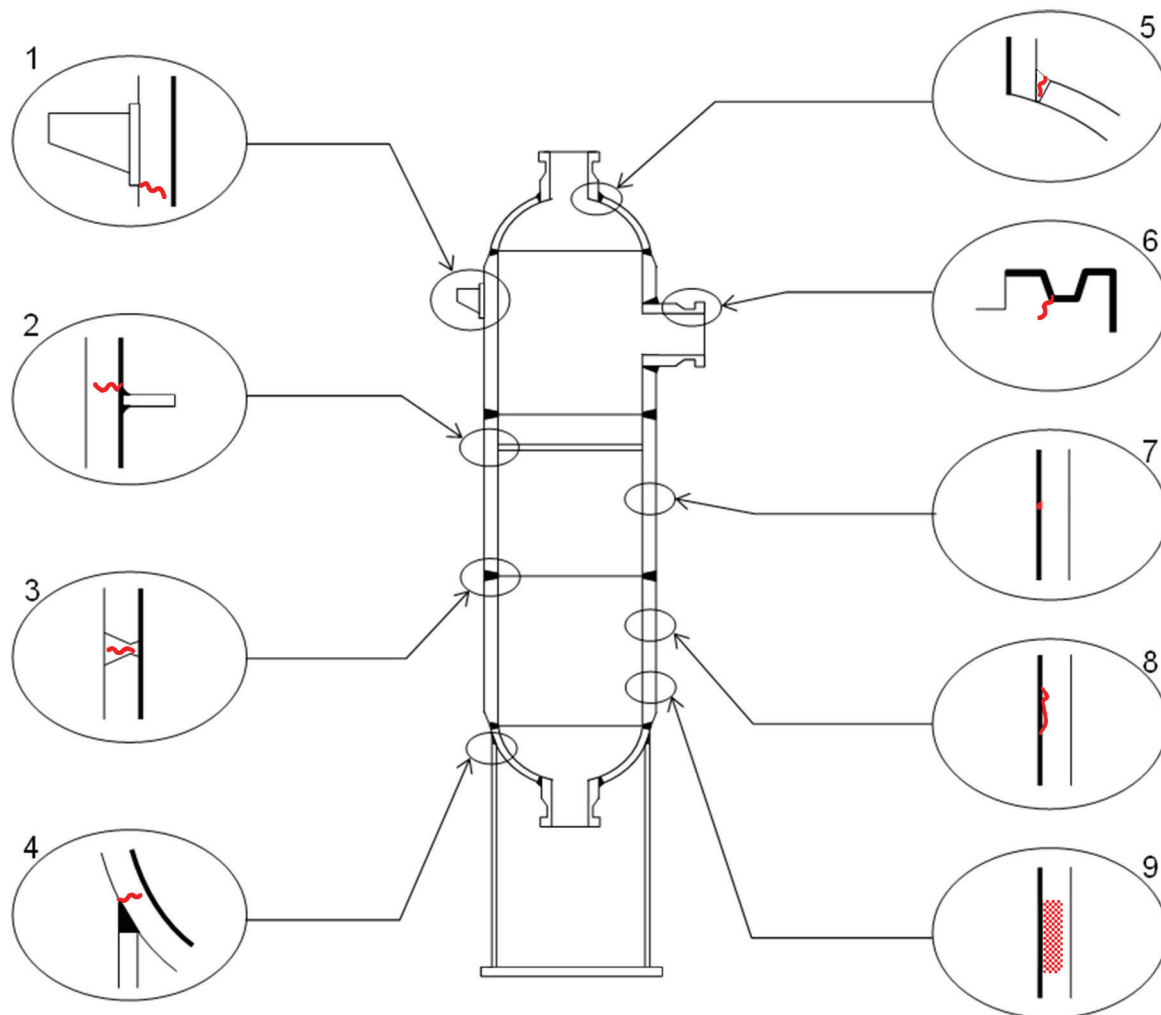
5.9 Thermal Fatigue Cracking of 300 Series Stainless Steel Weld Overlay

When a Cr-Mo reactor vessel with 300 series SS weld overlay cladding is heated up during operation and during a final PWHT, the 300 series SS expands more than the underlying Cr-Mo steel, resulting in thermal fatigue cracking. This results in stresses in the 300 series SS cladding that exceed the yield strength, resulting in residual tensile stress in the cladding when the reactor cools down.^[9] Thermal fatigue cracking typically occurs first at internal attachment welds that act as a stress concentration, as further discussed in 6.3. Experience also shows that this cracking is most pronounced in older Type 347 SS weld overlay deposits, which tend to have higher sigma phase levels. The effect of sigma phase level on cracking of SS overlay is further discussed in 5.4.^[9, 10, 12] In addition to sigma phase formation, it has been observed that Type 347 SS weld overlay with high levels of carbon and niobium can result in a very hard overlay deposit with limited fracture ductility and an increased susceptibility to cracking.^[9]

6 Flaws Found in Heavy Wall Reactor Vessels

6.1 General

There are several types of flaws that can occur in heavy wall reactor vessels, mostly occurring in older generation vessels. These are illustrated in Figure 2 (published in WRC 566) and further described in 6.2 to 6.12. These flaws can result from the combined effects of the damage mechanisms described in Section 5.



1. Cracks at external attachment welds (See 6.2)
2. Cracks at internal attachment welds (See 6.3)
3. Cracks at longitudinal and circumferential weld seams (See 6.4)
4. Cracks at skirt attachment welds (See 6.5)
5. Cracks at nozzle attachment welds (See 6.6)
6. Cracks at ring joint grooves (See 6.8)
7. Cracks in weld overlay cladding (See 6.9)
8. Cracks at the interface between the cladding and base metal (See 6.10)
9. Damage in the Cr-Mo base metal (See 6.12)

Figure 2—Areas Where Damage May Occur in Heavy Wall Reactor Vessels

6.2 Cracks in External Attachment Welds

Some reactors may have external attachments welded directly to the shell. Cracks may be caused by thermal stresses within or close to the external attachment welds. Thermal stresses at external attachments typically are caused by poor application of insulation in the area around the attachment. If the attachment is not fully insulated or insulation covered, it can act as a cooling fin, causing a high temperature gradient at the attachment, particularly during a heavy rain or snow. This can result in high thermal stresses. It is important that insulation and metal jacketing is properly reapplied after inspection of attachments is performed. As part of a thorough root cause analysis (RCA) in the event of crack-like flaw discovery, detailed fatigue evaluations based on heat transfer and thermal stress analyses have been employed to understand the impact of local cooling on the potential for fatigue-induced cracking.

6.3 Cracks at Internal Attachment Welds

Cracks are commonly found at 300 series SS internal attachment welds, such as to catalyst bed support rings, beam support pedestals, or outlet collectors. Figure 3 shows typical cracking in the weld overlay associated with an internal support ring. These surface-initiating cracks frequently propagate through the SS weld overlay, but seldom propagate deeply into the underlying base metal. A 300 series SS weld overlay is susceptible to cracking due to the difference in the coefficient of thermal expansion between the 300 series SS and underlying Cr-Mo steel as discussed in 5.4 and 5.9.^[9, 10, 12] During each startup and shutdown cycle, 300 series SS will experience very high stresses, typically well above the yield stress. These stresses will be tensile once the reactor has cooled from a high operating temperature. Cracking occurs at corners on internal support rings, pads, collectors, and other attachments because of the stress concentration that exists at these locations.

Type 347 SS weld overlay is commonly used for at least the outer layer of weld overlay in heavy wall reactors. Experience has shown that the Type 347 overlay in many older reactors is more susceptible to cracking because of a higher level of delta ferrite in the microstructure. During PWHT, delta ferrite transforms to sigma phase, which reduces overlay ductility. The chemical composition of the Type 347 weld consumables commonly used in older reactor vessels promotes higher levels of delta ferrite in the overlay. While this is beneficial for resistance to hot cracking during welding, the resulting weld overlay and attachment welds are more susceptible to cracking from the repeated thermal stresses associated with startup and shutdown cycles.

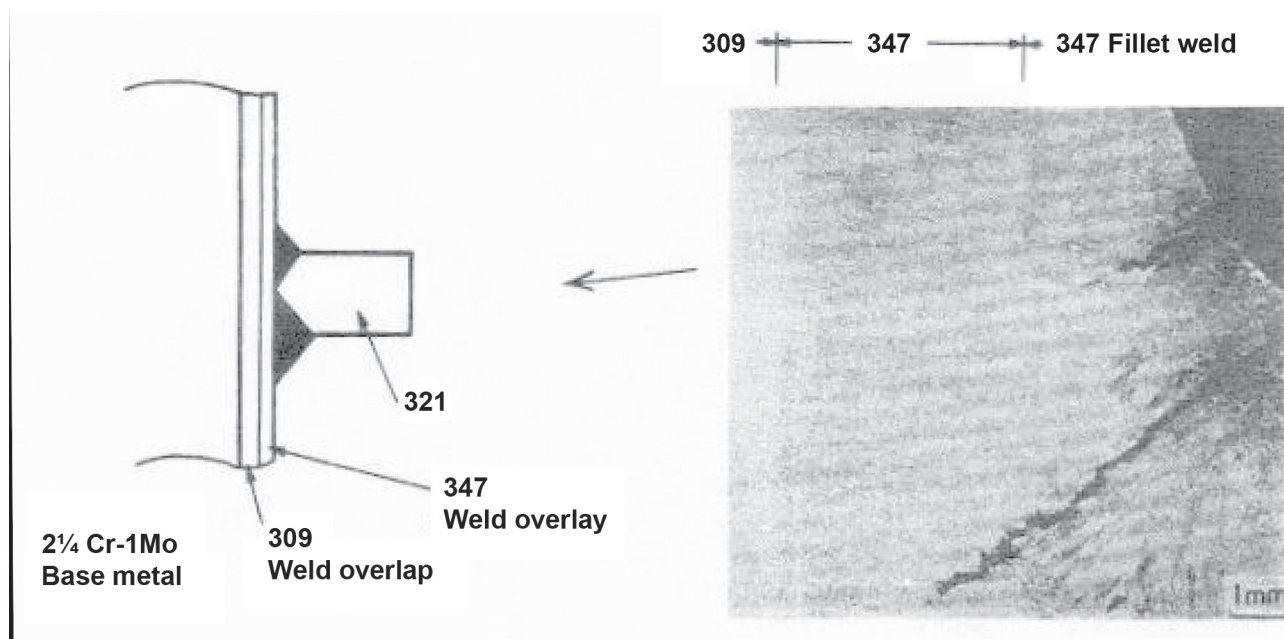


Figure 3—Metallographic Cross Section Showing Cracks in the Stainless Steel Weld Overlay in the Corner of an Internal Support Ring

6.4 Cracks in Longitudinal/Circumferential Weld Seams

Weld flaws, such as small hot cracks or lack of sidewall fusion, can form during fabrication. These types of weld flaws are normally embedded beneath external surfaces and are more common in older reactor vessels. These older reactors were inspected by radiographic testing (RT), which cannot routinely detect these types of planar flaws. Starting in the late 1980s, ultrasonic testing (UT) techniques have been used to more effectively inspect welds in reactor vessels. UT techniques have a greater ability to detect embedded planar flaws when compared with inspection using RT. As a result, welds in newer reactors inspected using UT techniques during fabrication rarely display the embedded planar flaws that were commonly found in older reactors. Many older reactors, in which the welds were originally inspected using RT, were later reinspected using UT techniques to examine the welds. These reinspection efforts using UT technology found many embedded flaws in these older reactors.

Figure 4 shows an example of an embedded flaw that was found at a weld in a reactor that was retired from service. In this case, the metallographic examination does display indications that this crack may have grown during each operating cycle. This was the conclusion reached by the investigators who performed the laboratory examination.^[13] Some experts speculate that the observed embedded crack occurred entirely during fabrication, but others believe that it may have grown during the startup/shutdown cycles. This remains a controversial issue in the assessment of heavy wall reactor vessels.

As part of the JIP on Aging Reactors,^[16] two sets of laboratory tests were performed to determine if it is possible for embedded flaws in a reactor vessel to propagate during operating cycles, solely due to the buildup of molecular hydrogen pressure when the reactor cools to ambient temperature. The results of this testing showed that embedded cracks in a reactor did not grow during operating cycles, which is consistent with some UT examinations that have been performed on heavy wall reactors in the past. Repeated UT examinations were performed on several reactors after operating cycles to determine if any of the embedded flaws propagated in service. The results of these reinspections after operating periods indicated that the embedded flaws did not propagate during operation or the subsequent shutdown for these reactors.

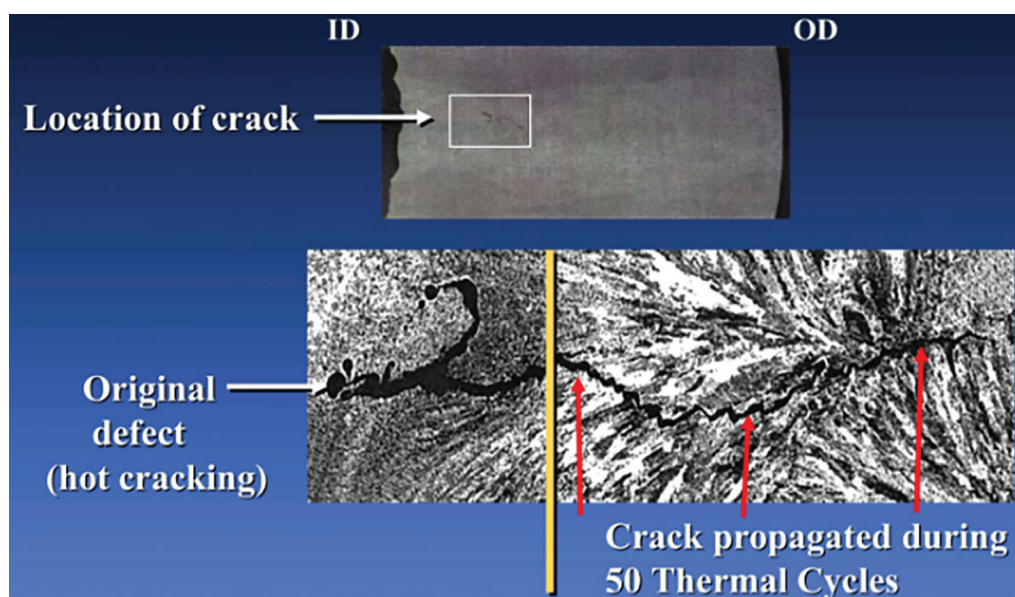


Figure 4—Embedded (Subsurface) Weld Flaw Depicted on a Metallurgical Cross Section^[13]

Embedded crack-like flaws in a heavy wall reactor vessel in high-temperature high-hydrogen pressure service are difficult to assess using conventional fitness-for-service (FFS) assessment procedures as included in API 579. In addition to conventional applied loads, it is necessary to consider the internal molecular hydrogen pressure that is applied when the reactor vessel cools. If equilibrium molecular hydrogen pressure levels are reached within the embedded flaw, it is likely that the calculated stress intensity will exceed threshold values for incremental crack growth resulting from hydrogen embrittlement.^[33] Because of this uncertainty, and based on feedback from NDE operators suggesting in-service propagation of some flaws, some reactor owners have decided to perform periodic inspections on embedded flaws to make sure the observed embedded flaws have not grown.

6.5 Cracks in Support Skirt Attachment Welds

Reactor vessels, especially older vessels, may have a support skirt welded directly to the bottom head. This situation has caused some concern for the possibility of cracks initiating at the toe or the root side of the welds due to the combined effects of the stress concentration at these locations and thermal stresses generated by the temperature gradient commonly occurring in this difficult-to-insulate geometry. Thermal stresses in support skirt attachment welds can be mitigated by the installation of an insulated “hot box” that minimizes temperature gradients at the support skirt connection to the vessel. In some recently fabricated heavy wall vessels, the support skirt connection consists of a forged ring that moves the attachment weld away from an area with high stresses generated by the thermal gradient.

It has been reported by several owners that cracking at the skirt attachment has not been observed in heavy wall reactor vessels. As a result, they do not routinely inspect for this type of cracking; however, this may be contingent on the type of skirt attachment design.

6.6 Cracks in Nozzle Attachment Welds

Flaws associated with nozzle attachment welds, such as lack of sidewall fusion, can originate during fabrication. Experience shows that these embedded fabrication flaws have, on a few occasions, appeared to have propagated during service or startup/shutdown cycles. However, as discussed in 6.4 regarding embedded crack-like flaws, the observed flaws normally are evaluated with an FFS assessment. Due to the uncertainty associated with addressing the buildup of molecular hydrogen pressure within an embedded flaw, some reactor owners have decided to perform periodic inspections on embedded flaws to make sure the observed embedded flaws have not grown.

6.7 Cracks in Quench Nozzles

Quench hydrogen is injected to maintain reactor bed temperatures and prevent excessive temperatures from the exothermic reaction that results from hydrotreating. Quench nozzle attachment areas can be prone to thermal fatigue cracking, especially if the nozzles are not equipped with a sleeve that runs through the nozzle (which is typically flanged to the internal distributor pipe) and distributes the cool quench hydrogen onto the catalyst bed. When the distributor piping lines the quench nozzle, it acts as a thermal sleeve that minimizes thermal stresses acting on the nozzle. In cases where stainless steel liners are improperly installed in nozzles, they typically fail after a short operating period.

In a quench nozzle without an internal distributor pipe inside the nozzle, the nozzle wall is exposed directly to cool hydrogen gas. In this situation, cracking initiates at the corner where the end of the set-in nozzle meets the ID surface of the reactor. It then propagates axially along the inside surface of the nozzle. This type of cracking is more common in reactor vessels with internal SS cladding due to the high thermal coefficient of expansion for 300 series SS compared with the underlying Cr-Mo steel. Examination for this cracking is typically performed from the inside surface of the reactor during a turnaround using PT for clad or overlayed vessels and MT for vessels without cladding. An example of thermal stress cracking observed on the inside surface of a vessel at a quench nozzle in a heavy wall reactor vessel is shown in Figure 5.

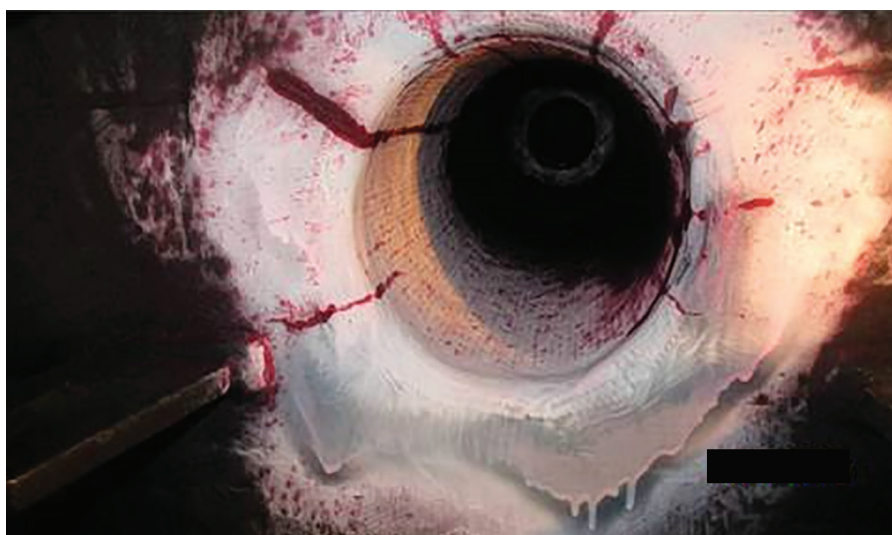


Figure 5—Cracking Observed at Quench Nozzle in a Heavy Wall Reactor Vessel

6.8 Cracks in the Ring-type Joint Gasket Grooves

Cracks have been found at the bottom corners of SS weld overlayed RTJ gasket grooves. Cracking typically has arrested in weld overlay, but in some cases, cracking has been found to propagate deeply into the base metal of the flange. Figures 6 and 7 show a typical crack in the corners of Type 347 SS weld overlayed RTJ gasket grooves.

Cracks have occurred on both the inside and outside corners of the groove, but tend to occur more frequently at the inside corner. Crack propagation is usually attributed to high stress concentration at the corners (especially if not properly radiused), temperature gradients through the flange, and high applied tensile stress in response to ring gasket compression. Crack initiation may also be caused by chloride SCC, and/or polythionic acid SCC during startup.

On heavy wall reactors that have experienced ring groove cracking, many owners have modified the flanges or flange faces to change the original ring joint configuration to a raised face using a flat compressed gasket. The raised face flanges are not prone to RTJ cracking. Raised face flanges are now commonly used for new reactor fabrication rather than RTJ flanges.

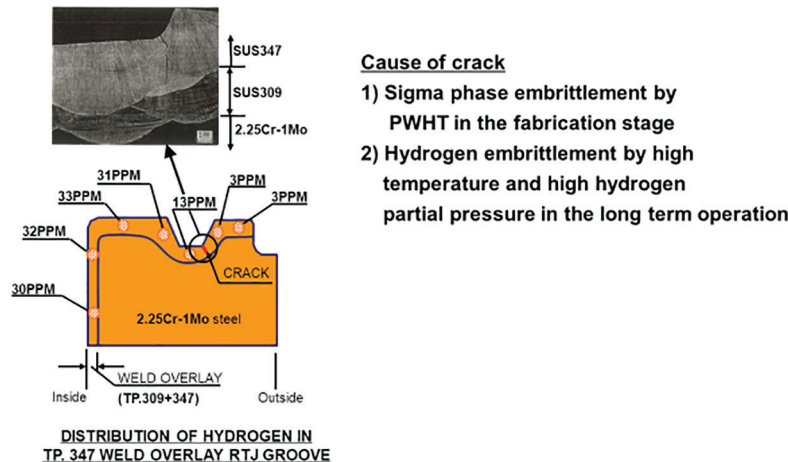


Figure 6—Cracks Associated with a RTJ Flange Typically Found at the Corner of the Groove



Figure 7—Cross Section of an RTJ Flange with Cracking from the Inner Corner that Extended Deeply into the Cr-Mo Base Metal

6.9 Cracks in SS Weld Overlay

Cracks have been found in 300 series SS weld overlay. These cracks can propagate through the weld overlay, but seldom propagate into the underlying Cr-Mo steel, with the exception of ring joint grooves as discussed in 6.8. This type of cracking is like cracking found at the corner of internal attachments as described in 6.3. The major difference is that the cracks found at the corner of internal attachments occur more readily because of the