

Impact of Hydrogen Embrittlement on Minimum Pressurization Temperature for Thick-wall Cr-Mo Steel Reactors in High-pressure H₂ Service—Initial Technical Basis for RP 934-F

API TECHNICAL REPORT 934-F, PART 1
FIRST EDITION, SEPTEMBER 2017



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EXECUTIVE SUMMARY

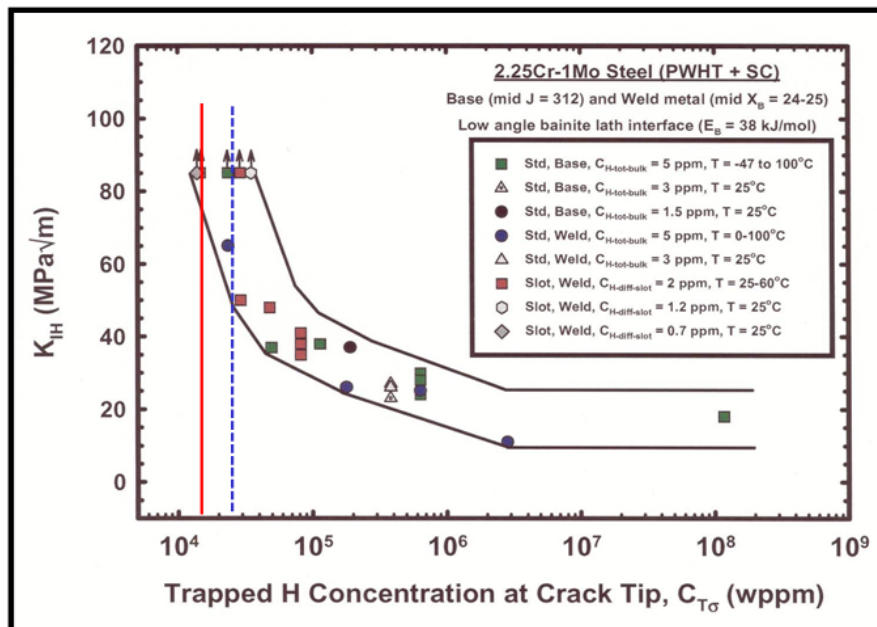
The objective of this study, in support of API Recommended Practice 934-F [*Guidance for Establishing a Minimum Pressurization Temperature (MPT) for Heavy Wall Reactors in High Temperature Hydrogen Service During Startups and Shutdowns*], is to establish the technical basis for determining a minimum pressurization temperature (MPT) necessary to avoid internal hydrogen-assisted cracking (IHAC) of weld metal and base plate of temper embrittled 2¼Cr-1Mo steel in high-pressure H₂ service. The threshold condition for the onset of subcritical crack propagation—and its dependencies on dissolved hydrogen concentration, temperature, and steel purity/temper embrittlement—are targeted as particularly important to pressure vessel safe operations. A second objective is to improve the underlying data base for fracture mechanics fitness-for-service (FFS) modeling of IHAC. Both analyses are built on the conservative rising displacement threshold stress intensity factor for IHAC (K_{IH}).

This investigation has accomplished five tasks, leading to the following conclusions and key figures taken from the body of this report. These conclusions are sufficient to establish the API 934-F section on MPT to conservatively avoid IHAC in 2¼Cr-1Mo steel.

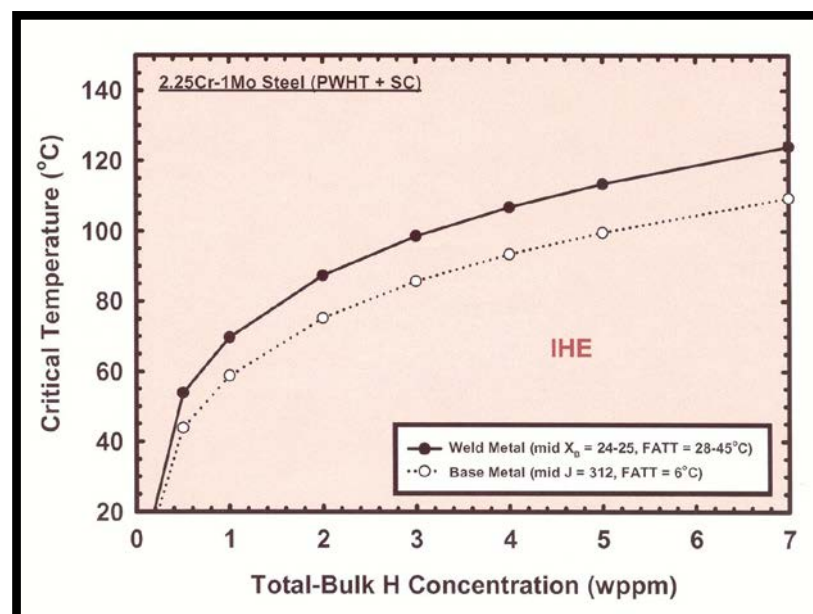
Task 1.0—Summarize and clarify the technical approach, assumptions, data, and modeling results used in Phase II JIP research to quantitatively establish the H concentration and temperature dependencies of the threshold stress intensity, K_{IH} , for IHAC and the concentration dependence of MPT for moderate-impurity 2¼Cr-1Mo steel.

- 1) Measured threshold stress intensity factor (K_{IH}) for the onset of IHAC increases with decreasing bulk-dissolved H concentration and increasing temperature, as proved by experimental results for multiple specimen geometries of 2¼Cr-1Mo steel.
- 2) The H concentration and temperature dependencies of K_{IH} are explained physically by the interactive effect of each variable on the concentration of H ($C_{T\sigma}$) that is enhanced at a reference location in the crack tip fracture process zone due to localized hydrostatic stress and microstructure sites for H trapping that constitute the crack path.
- 3) The steps necessary to predict $C_{T\sigma}$ as a function of total dissolved H concentration and temperature, proposed by Al-Rumaih in a joint industry program (JIP) Phase II PhD study at the University of Virginia, are validated as fully correct and are clarified to provide the scientific basis for engineering applications that seek to avoid IHAC. This analysis was guided by mechanistic consideration of H trapping and embrittlement in the crack tip region of a complex steel microstructure.

- 4) A master experimental correlation exists between measured K_{IH} and diffusion-model-predicted $C_{T\sigma}$ for moderate-purity temper embrittled [$6^\circ\text{C} < \text{fracture appearance transition temperature (FATT)} < 43^\circ\text{C}$] 2½Cr-1Mo, including a critical level of locally trapped H below which K_{IH} rises toward K_{IC} ($C_{T\sigma\text{-CRIT}}$). The critical H concentration is marginally lower for weld metal compared to base plate, with each microstructure temper embrittled by laboratory step cooling. Figure 15 follows, specific to $C_{T\sigma}$ predicted at 2CTOD ahead of the crack tip; $\delta_{FPZ} = 9\ \mu\text{m}$:

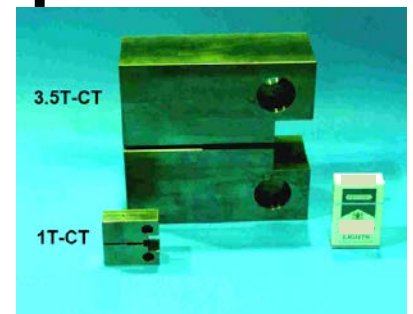
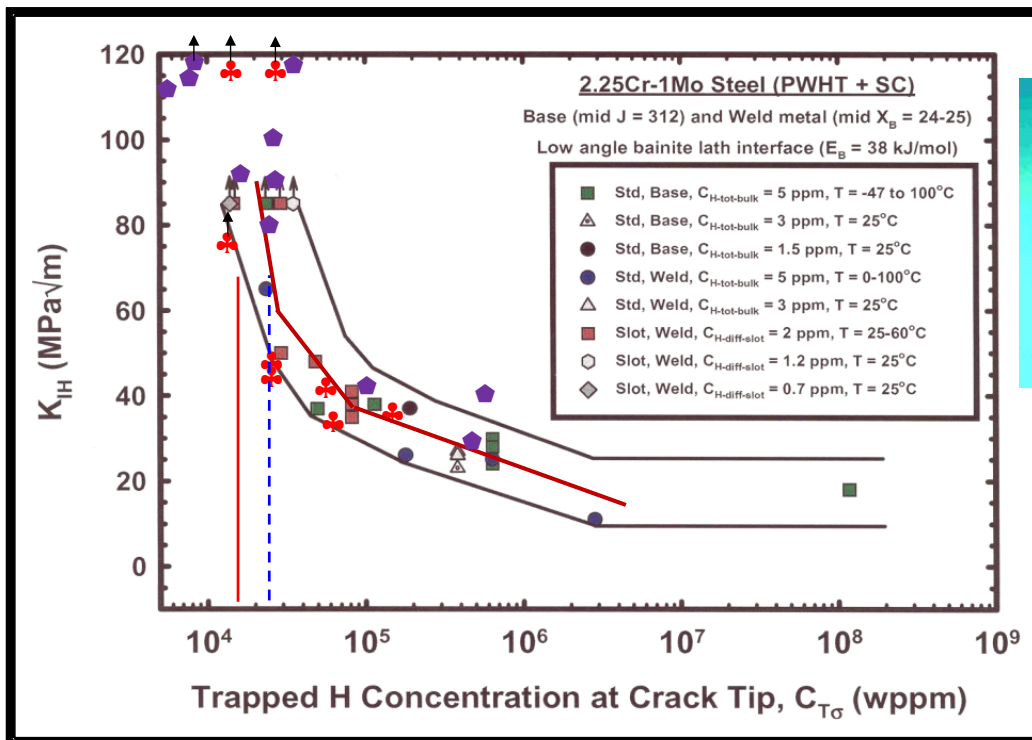


- 5) The master K_{IH} vs $C_{T\sigma}$ correlation provides the basis for a critical temperature, T_{CRIT} , above which IHAC is not observed and that is the foundation for MPT determination. The T_{CRIT} increases with increasing $C_{H\text{-Total}}$ dissolved in the “structure” at high temperature, with a quantitative dependence reported in Phase II work specific to the compact tension geometry and moderate-FATT 2½Cr-1Mo weld metal and base plate. Figure 16 follows based on K_{IH} vs $C_{T\sigma}$ in Figure 15. Diffusion analysis (see Task 4.0) is required to apply this specific result to a cracked reactor vessel in H_2 service.



Task 2.0—Validate the Phase II correlation of K_{IH} and critical temperature vs H concentration, based on new analyses of post-Phase-II IHAC data.

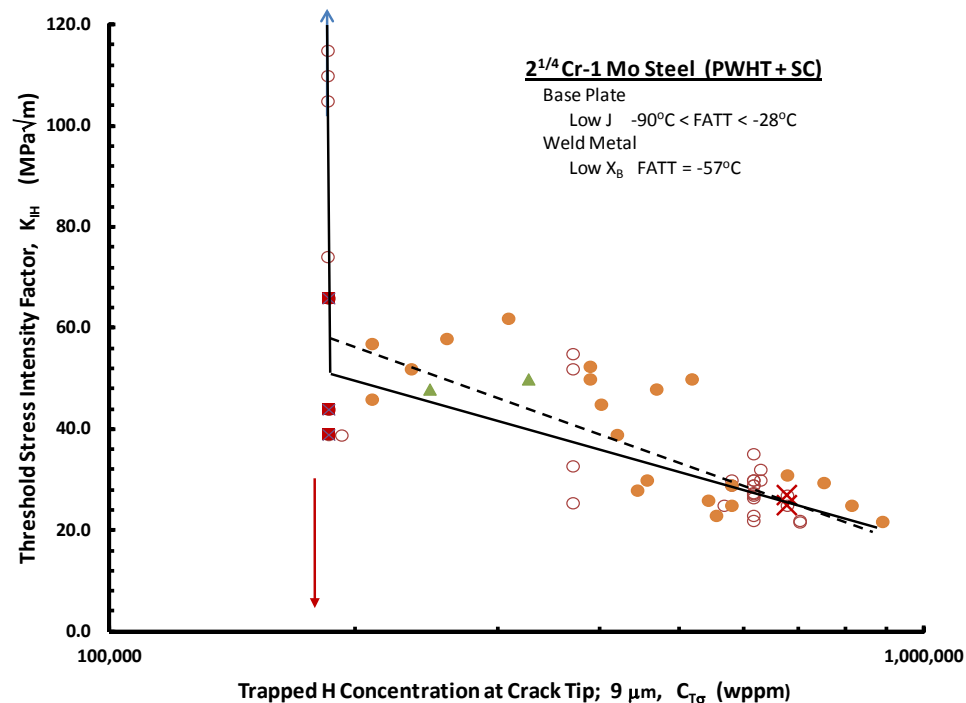
- 1) Japanese experiments with unusually thick and H_2 -precharged compact tension specimens of moderate-purity temper embrittled $2\frac{1}{4}Cr-1Mo$ weld metal and base plate ($22^\circ C < FATT < 43^\circ C$) quantitatively validate the master correlation between K_{IH} and $C_{T\sigma}$. Figure 21 follows showing agreement between these thick-specimen results (♣, ◆) and the small-specimen master curve from Figure 15, each related to $\delta_{FPZ} = 9 \mu m$:



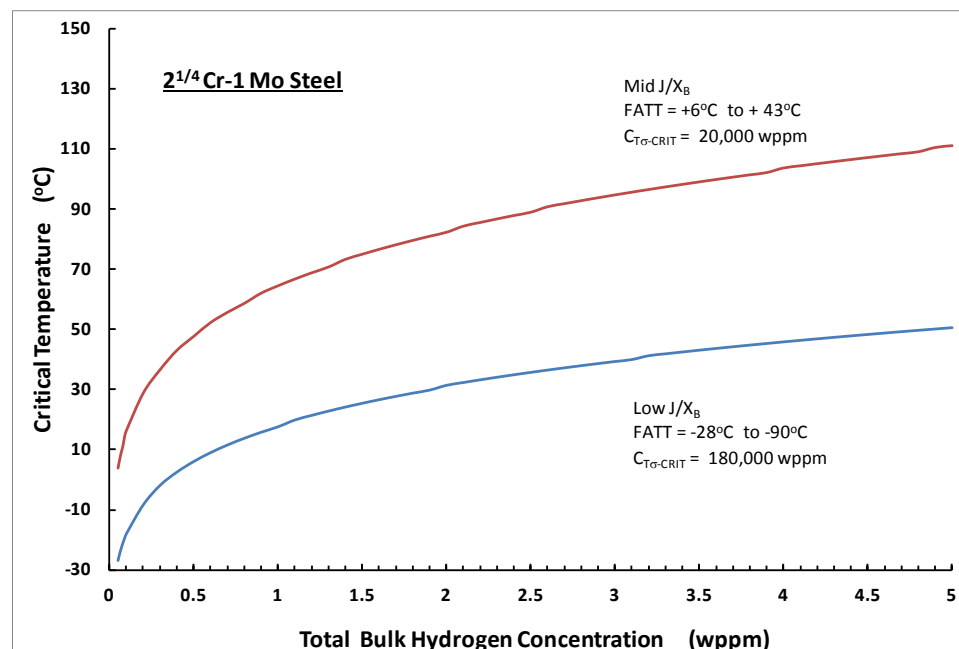
Task 3.0—Enhance the Phase II analysis of K_{IH} vs crack tip H concentration, and thus MPT, by describing the interaction between temper embrittlement and IHAC using JIP Phase I data so as to predict the influence of modern steel purity.

- 1) Results of extensive JIP Phase I IHAC experiments, conducted with H_2 -precharged compact tension specimens of multiple high-purity lots of laboratory step-cooled $2\frac{1}{4}Cr-1Mo$ weld metal and base plate ($-90^\circ C < FATT < -28^\circ C$) are well correlated by a master correlation between K_{IH} and $C_{T\sigma}$, as verified by additional literature K_{IH} data.

- 2) The critical level of $C_{T\sigma}$, $C_{T\sigma-CRIT}$, below which K_{IH} rises toward K_{IC} for IHAC increases with increasing resistance to Cr-Mo temper embrittlement, or decreasing FATT. The master correlation for modern low-FATT 2 $\frac{1}{4}$ Cr-1Mo is shown in Figure 28 for $\delta_{FPZ} = 9 \mu\text{m}$:

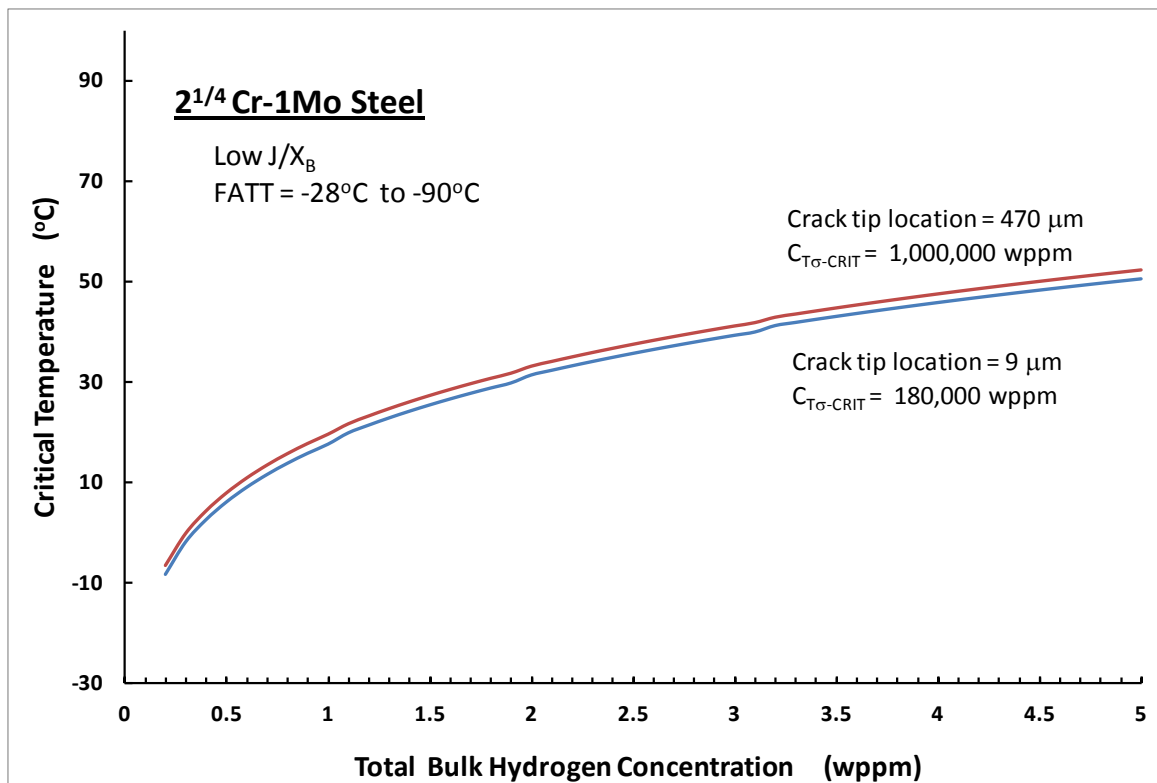


- 3) The critical temperature for elimination of IHAC, predicted as a function of the dissolved total H concentration in a compact tension specimen, falls with increasing steel purity, which results in decreasing temper embrittlement and decreasing FATT. Figure 29 follows; diffusion analysis (see Task 4.0) is required to apply this result to a cracked reactor vessel in H_2 service:



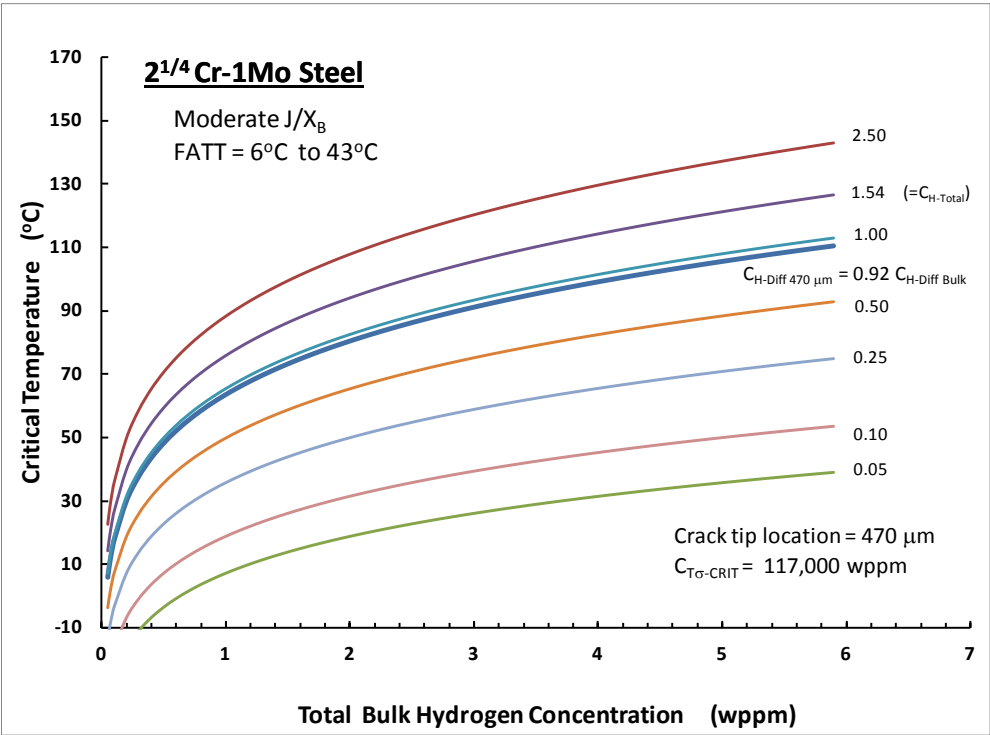
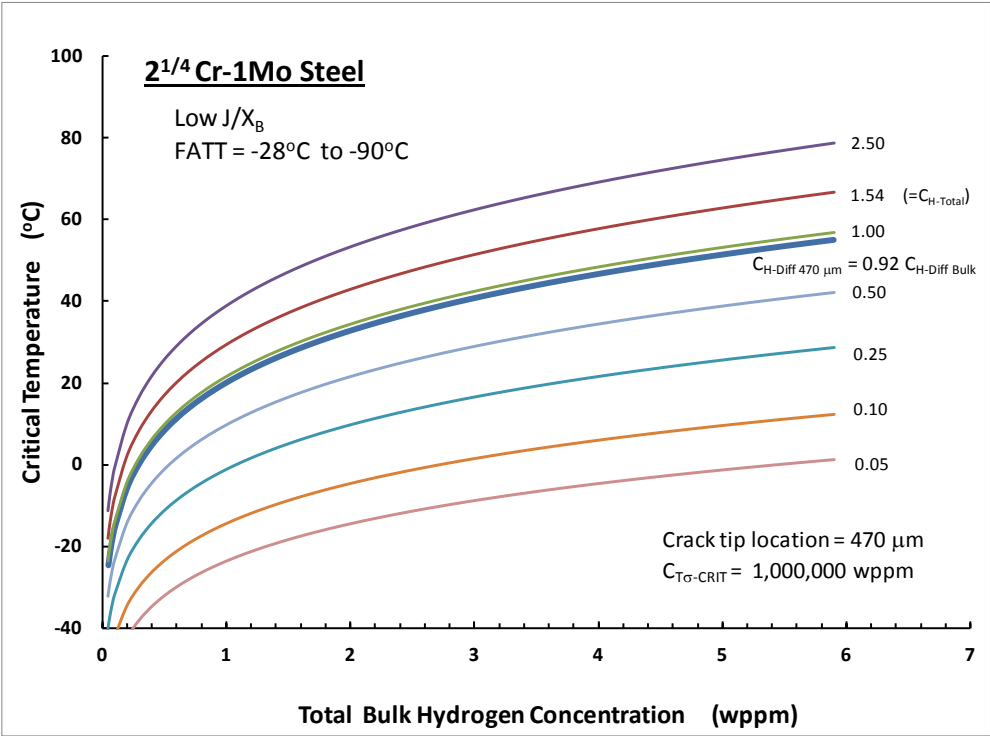
-
- 2^{1/4}Cr-1Mo Steel**
- Mid J/X_B
 FATT = +6°C to +43°C
 C_{TO-CRIT} = 20,000 wppm
- No IHAC
- IHAC
- Critical Temperature (°C)
- Crack Tip Diffusible H Concentration @ 9 μm (wppm)

- 1) Following the Al-Rumaih–Gangloff (AG) work in Phase II, a crack tip H concentration similitude parameter is proposed; equal levels of K_{IH} are associated with equal $C_{T\sigma}$ such that the master correlation of K_{IH} and $C_{T\sigma}$ provides a physically justified basis for MPT determination and broader FFS modeling of reactor vessels in high-pressure H_2 service. The H concentration similitude parameter can be related to one of several locations proximate to a crack tip.
- 2) Essentially identical MPT and K_{IH} predictions are provided for H localization at either a very close crack tip reference location ($\delta_{FPZ} = 9\mu m$, as developed in Tasks 1.0 to 3.0) or a location ($\delta_{FPZ} = 470\mu m$) on the order of the crack tip plastic zone size for a typical level of K_{IH} . See Figure 35, which is relevant to the compact tension specimen geometry:



- 3) A diffusion analysis of the sort enabled by REACT, or a separate ABAQUS-type model, is necessary to define local H concentration ($C_{T\sigma}$) for a given reactor operating history and crack tip location. This flexibility in crack tip location for $C_{T\sigma}$ determination simplifies this diffusion problem. Nonetheless, the relationship between known bulk $C_{H\text{-Total}}$ and the crack tip H concentration similitude parameter must be considered for MPT determination. Use of the compact-tension-based relationship between $C_{H\text{-Total}}$ and T_{CRIT} (e.g. Figures 16 and 29) will lead to a conservative overprediction of MPT provided that the diffusible H concentration at the crack tip position in a structure is less than the value typical of this location in the compact tension specimen. If the converse is true, then the MPT value inferred from the compact tension will be nonconservative.
- 4) This behavior in Item 3) is captured by a set of MPT vs $C_{H\text{-Total}}$ trends lines that provide engineering estimates of MPT, for both modern (low-FATT, Figure 37) and temper embrittled (moderate-FATT, Figure 38) 21/4Cr-1Mo weld metal and base plate, and that simplify the H diffusion analysis.

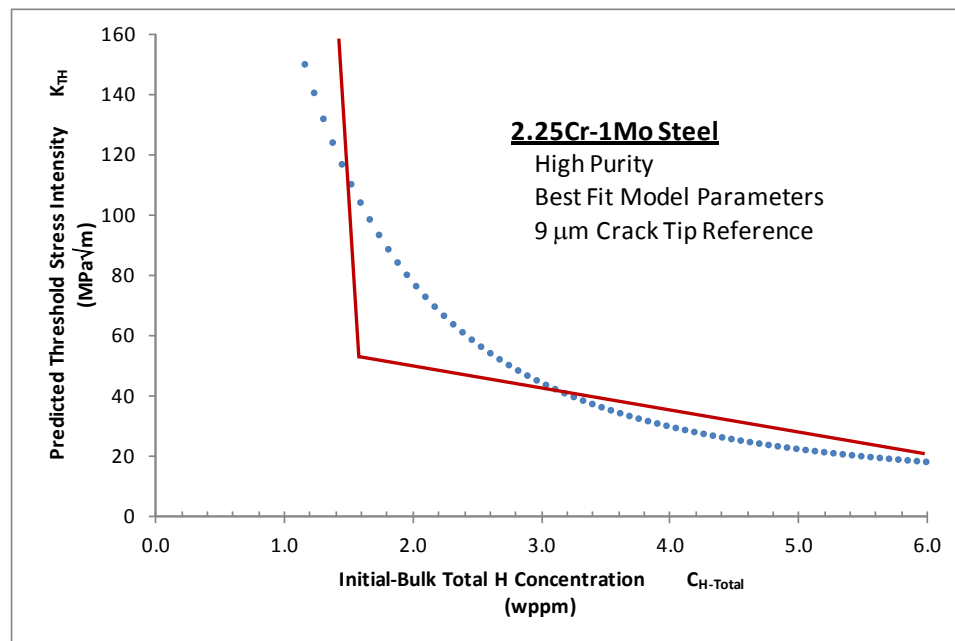
RECOMMENDATION—The following two plots should be used in API 934-F to develop an MPT to avoid H cracking in a reactor wall, rather than the compact-tension-based prediction presented in the early work by Al-Rumaih, which is shown by the lines marked ($C_{H-Diff\ 470\ \mu m} / C_{H-Diff\ Bulk}$). A detailed procedure to use these plots is presented in Task 4.0 of this report.



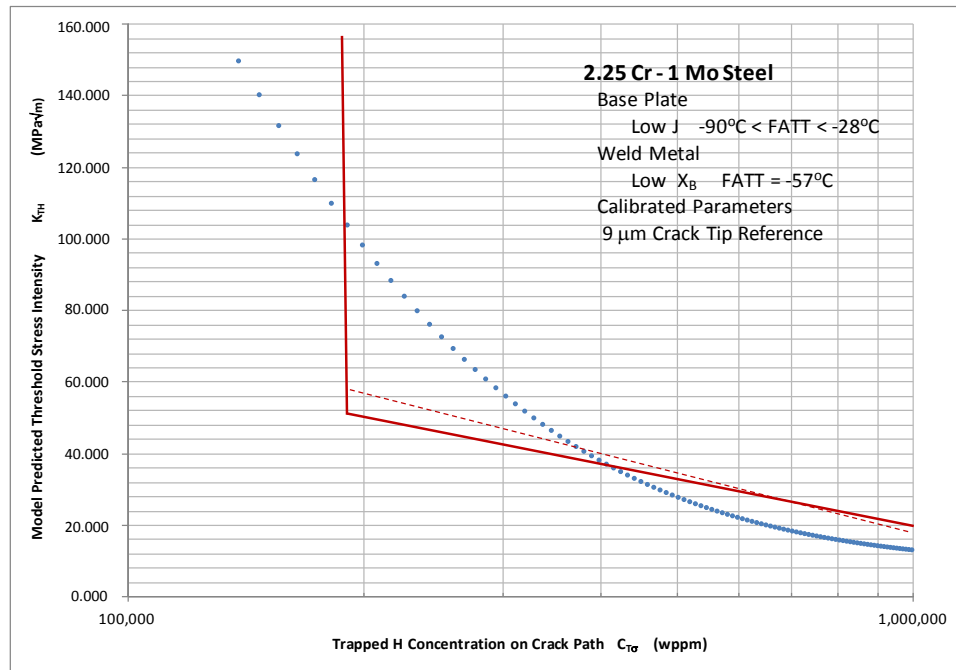
- 5) An engineering method for MPT determination, proposed by Anderson and based on crack tip H concentration similitude, provides essentially the same predictions of MPT as the present model embodied in Figures 37 and 38. This is expected since both the Anderson–Brown (AB) and AG approaches are based on the same crack tip similitude concept and JIP Phases I and II laboratory data.
- 6) Taken *in toto*, the master correlations between K_{IH} and $C_{T\sigma}$ are sufficient to predict MPT vs total dissolved H concentration ($C_{H-Total}$) that is available for diffusion to a crack tip in a reactor pressure vessel. This analysis predicts MPT values for moderate-purity temper embrittled steels (with FATT on the order of 40 °C) to be in the range of 60 °C to 110 °C for $C_{H-Total}$ between 1.0 and 5.0 wppm. The predicted MPT is lower for higher-purity Cr-Mo steels (with FATT on the order of –60 °C); 15 °C to 50 °C for total dissolved H concentrations between 1.0 and 5.0 wppm.
- 7) These relatively low levels of required MPT are less than typical temperatures that are dictated by classical considerations of MPT to avoid cleavage fracture in temper embrittled Cr-Mo steels. That is, current reactor vessel operations and MPT guidance do not need to be altered by increased MPT to avoid IHAC, unless the severity of such hydrogen cracking exceeds that typical of the low- to moderate-FATT steels considered in this analysis.

Task 5.0—Validate the empirically based trends and predictions of the effects of temperature and steel purity on the threshold stress intensity through consideration of state-of-the art theory and micromechanical modeling of IHAC.

- 1) The master correlation between K_{IH} and $C_{T\sigma}$, as well as the detrimental effect of temper embrittlement, are explained by theoretical modeling of the threshold stress intensity for IHAC. Such modeling leverages necessarily limited material property experiments to enhance the capability to predict K_{IH} vs H concentration as well as MPT. See Figure 57, with K_{IH} predicted (dotted) and measured (solid) vs $C_{H-Total}$:



and Figure 58 with K_{IH} predicted (dotted) and measured (solid) vs $C_{T\sigma}$ at $\delta_{FPZ} = 9 \mu\text{m}$, each for modern low-FATT Cr-Mo steel:



- 2) Current damage-mechanism-based modeling does not distinguish between the quasi-static and rising crack mouth opening displacement values of threshold stress intensity factor, K_{TH} and K_{IH} , respectively. Moreover, uncertain input parameters are necessary for modeling of K_{IH} vs $C_{H-Total}$, temperature, and steel temper embrittlement. Experiments are necessary to calibrate several of these parameters.

Impact of Hydrogen Embrittlement on Minimum Pressurization Temperature for Thick-wall Cr-Mo Steel Reactors in High-pressure H₂ Service—Initial Technical Basis for RP 943-F

1 BACKGROUND

Over the past 15 years, two major joint industry programs (JIPs) focused on the deleterious effect of hydrogen embrittlement, interacting with temper embrittlement, on fitness-for-service (FFS) of thick-wall Cr-Mo steel pressure vessels that operate for long times in high-pressure, high-temperature gaseous hydrogen environments. Such vessels undergo shutdown–startup cycles that penetrate the temperature regime where internal hydrogen-assisted cracking (IHAC) could occur from supersaturated hydrogen (H) trapped in the microstructure as a result of the high temperature exposure in H₂. Pressure vessel safety, as well as economic operation, may be compromised by:

- a) accumulation of increments of subcritical cracking due to IHAC over multiple shutdown cycles; and
- b) the reported potential for larger-scale cracking due to H-reduced plane strain fracture toughness in the ductile-to-brittle (cleavage) transition temperature regime and stable-tearing resistance in the upper shelf regime.

The goal of the Phase I JIP program was to establish the laboratory test method and data base to quantify the effects of steel composition/temper embrittlement, weld metal vs base plate microstructure, dissolved hydrogen concentration, and temperature on the stress intensity factor threshold and crack growth rates for subcritical IHAC in 2¼Cr-1Mo steel ^[1]. Three participating laboratories conducted over 80 complex experiments to quantify IHAC for FFS modeling. A key aspect of this work was examination of 10 base plate and weld metal compositions in the 2¼Cr-1Mo class, spanning a range of impurity content represented by the commonly used J-factor and X_B parameter and subjected to either laboratory step cooling or long-term in-service exposure. A parallel program, conducted by Dr. Ted Anderson (Quest Reliability LLC), developed a damage-tolerant fracture mechanics software tool (REACT) to predict FFS, focused on IHAC and utilizing the stress intensity (K) analyzed data base produced in Phase I laboratory work.

Phase I research demonstrated the occurrence of severe IHAC of Cr-Mo weld metal and base plate, associated with three loading modes:

- 1) threshold stress intensity, K_{TH} , for the arrest of IHAC growth under quasi-static displacement and thus decreasing K, plus associated subcritical crack growth rates (da/dt);
- 2) threshold stress intensity, K_{IH} , for the onset of subcritical IHAC growth under slow-rising crack mouth opening displacement (CMOD) and thus slow-rising K, plus da/dt; and
- 3) reduction in fracture toughness, K_{IC-H} , for stable-tearing or unstable growth under relatively higher rate loading. This fracture-toughness-based behavior is not considered in the present work.

Figure 1 (top) shows the important finding that, while K_{TH} for IHAC rises with decreasing steel strength, K_{IH} is nearly strength independent and is particularly low relative to the plane strain fracture toughness, K_{IC} . Figure 1 (bottom) illustrates typical measured subcritical da/dt for rising vs fixed CMOD; when the rising CMOD was fixed at a high K level, da/dt rapidly fell to below measurement resolution. Phase I established that the dramatic difference in cracking behavior shown in Figure 1 is not an experimental artifact, but rather due to an uncertain H microstructure–strain interaction leading to cracking, or to local crack tip driving force change relative to R-curve-type stable crack growth behavior. This work then characterized K_{IH} as well as da/dt as a function of steel temper embrittlement, dissolved H concentration, temperature, and loading rate stated as dK/dt. Algorithms were developed for use in REACT. Examples shown in Figures 2 and 3 indicate that K_{IH} rises with decreasing total H concentration measured by vacuum extraction at 600 °C ($C_{H-Total}$), increasing steel purity in the presence of laboratory step cooling to simulate temper embrittlement, and increasing

temperature. Phase I experiments showed that rising CMOD IHAC was capable of producing centimeters of slow crack growth in Cr-Mo steel, suggesting that this damage mode must be considered in pressure vessel FFS management. More extensive data from this Phase I research are presented and analyzed in Tasks 1.0, 2.0, and 3.0.

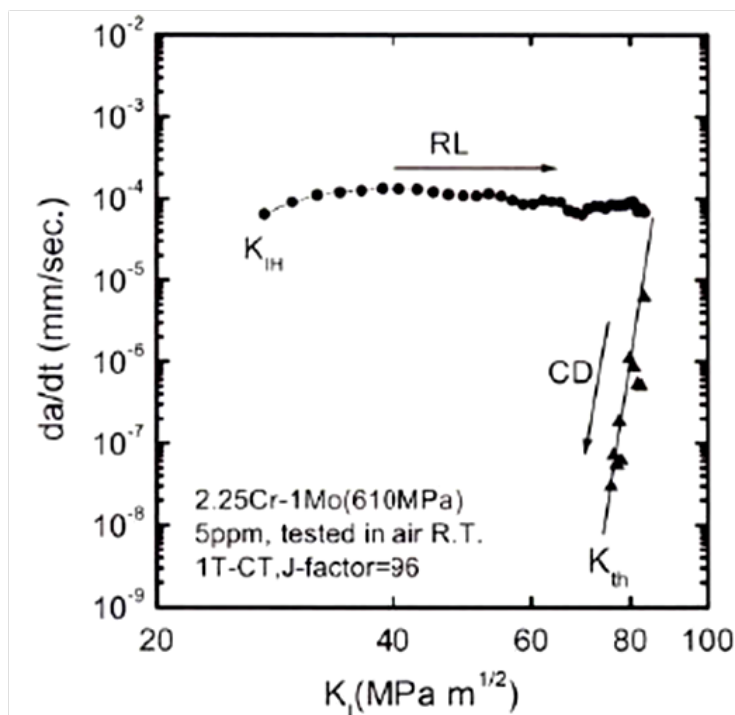
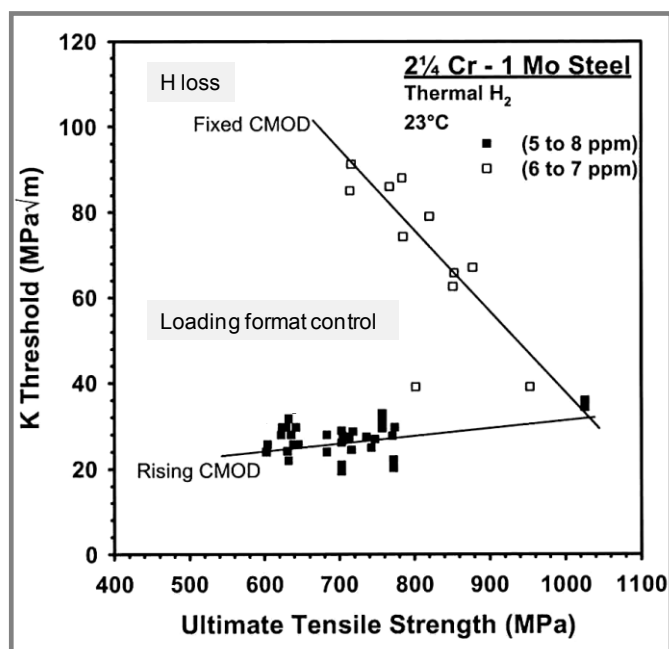


Figure 1—Effect of loading format on: (top) the threshold for IHAC^[1] and (bottom) the growth rate vs stress intensity factor relationship for a modern pure 2 1/4Cr-1Mo steel containing 5 wppm predissolved H ($C_{H-Total}$) and stressed at 23 °C [unpublished, Wada and Tanaka (Japan Steel Works), 2003].

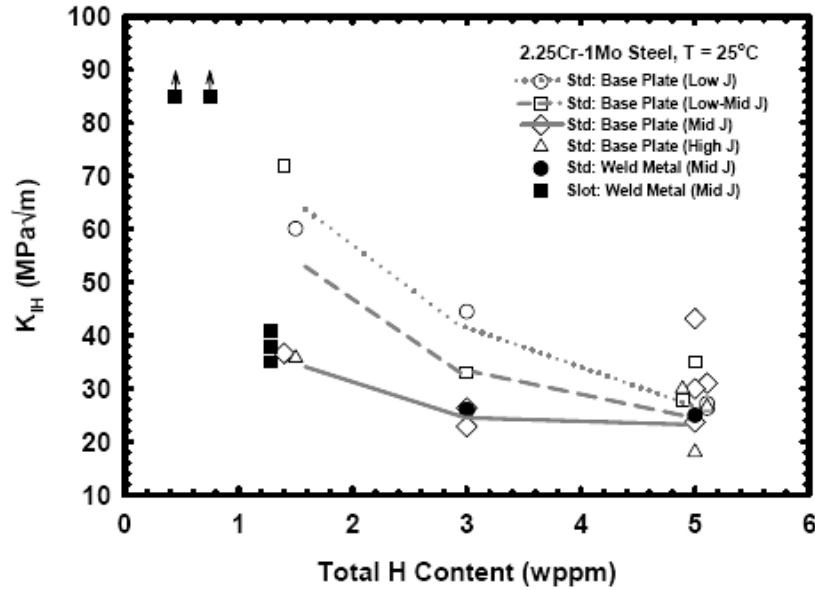


Figure 2—The effect of measured predissolved total H concentration ($C_{H-Total}$) on K_{IH} for the onset of IHAC under rising CMOD ($dK/dt = 0.007 \text{ MPa}\sqrt{m}$) for laboratory step-cooled 2 $\frac{1}{4}$ Cr-1Mo base plate and weld metal of several purity levels and tested at 23 °C^[1]. The results for the “Slot Weld Metal” are detailed in an ensuing section with values of $C_{H-Total}$ computed from a 3-D diffusion analysis of this novel specimen geometry^[2].

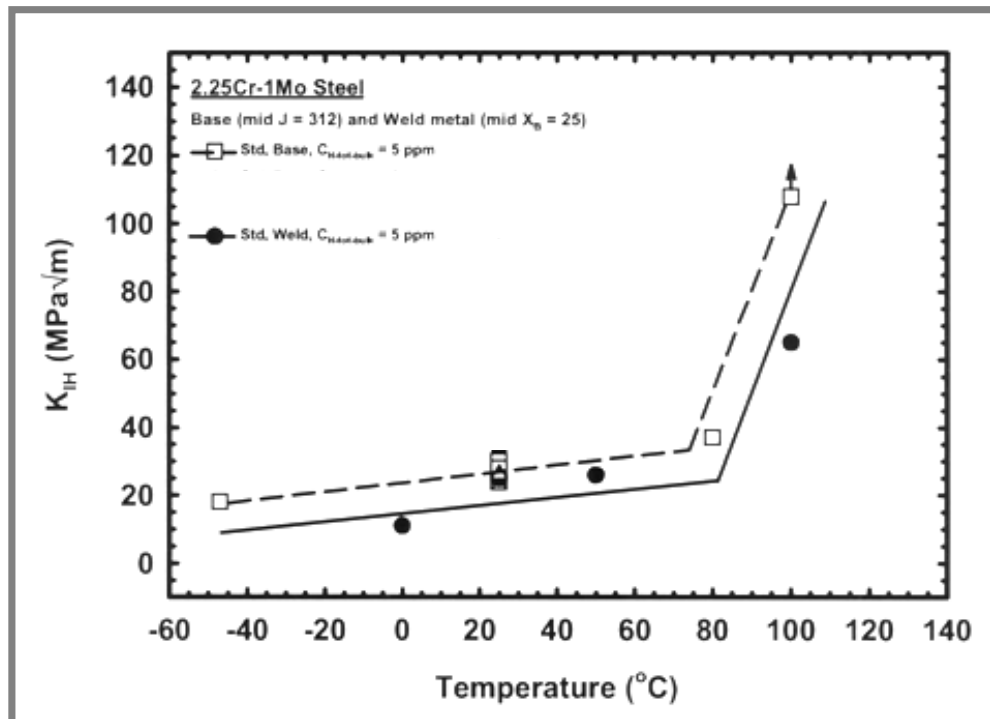


Figure 3—The effect of test temperature on K_{IH} for the onset of IHAC under rising CMOD ($dK/dt = 0.007 \text{ MPa}\sqrt{m}$) for 2 $\frac{1}{4}$ Cr-1Mo base plate and weld metal of moderate purity and a single $C_{H-Total}$ of 5 wppm^[1].

The beneficial effect of increasing temperature, above a critical level, in reducing IHAC (Figure 3) is central to determination of a safe minimum pressurization temperature (MPT) to avoid hydrogen embrittlement. A major uncertainty associated with the data obtained in Phase I was loss of H during slow loading at the elevated temperatures illustrated in Figure 3. All surfaces of the fracture mechanics specimens were gold plated to minimize H loss; however, measurements showed that the gold plate was not consistently effective, and moreover, H may have been lost from the crack tip that was barrier free as a result of fatigue precracking before H charging and plating.

Phase II JIP research was conducted with the objectives of:

- a) correcting these deficiencies,
- b) quantitatively characterizing the effect of temperature on K_{IH} , da/dt , and K_{TH} for IHAC in a 2¼Cr-1Mo steel as inputs for REACT modeling, and
- c) understanding the physical origin of reduced IHAC with increasing temperature ^[2].

The Phase II approach was centered on development of the modified fracture mechanics specimen shown in Figure 4. Hydrogen was produced electrochemically on slot surfaces and available for diffusion to the crack tip, with a steady state established prior to specimen loading. This H diffusion was modeled in three dimensions by a finite element analysis (FEA). Crack growth was measured continuously during loading with a high-precision direct current electrical potential system ^[2]. The elastic-plastic stress intensity solution for this specimen was developed. Results obtained for specially melted weld metal of legacy 2¼Cr-1Mo composition confirmed severe IHAC produced by active rising CMOD, consistent with K_{IH} and da/dt data from conventional experiments carried out during Phase I. For example, the filled circle data presented in Figure 5 show that da/dt rises during rising CMOD, but immediately falls during fixed CMOD, only to rise again when the CMOD rise is restarted. The fixed triangle and filled square points show the reproducibility of the rising CMOD data, without fixed CMOD holding. The open circles show crack growth rates for fixed CMOD loading, with K falling from a high level. The slotted-specimen data contained in Figure 6 show that K_{IH} rises with increasing temperature, consistent with the gold-plated specimen experiments from Phase I. These data show that the precise temperature dependence of K_{IH} depends on H concentration. This point is developed in detail in Task 1.0 as the basis for MPT prediction.

The effect of the rate of rising K prior to the onset of IHAC at K_{IH} can affect IHAC threshold and rate properties. Phase I data showed that K_{IH} is insensitive to dK/dt for values as high as 0.4 MPa√m/s (see Figure 7); a standard rate of 0.007 MPa√m/s was adopted as a conservative standard for laboratory testing of all 2¼Cr-1Mo weld metal and base plate purities studied in Phase I. Nonetheless, in characterizing the effects of H concentration and temperature on K_{IH} , it is important to consider the rate of loading, dK/dt . This issue is particularly important for those values of these variables that result in higher resistance to IHAC ^[1]. The Phase I data are insufficient to prove that dK/dt in the range of 0.001 to 0.01 MPa√m/s provides a conservative lower bound on the threshold for IHAC. That is, if K_{IH} rises with increasing temperature above 23 °C, for a loading rate of 0.007 MPa√m/s, there is no experimental guarantee that this elevated K_{IH} is within the lower bound plateau regime. However, the mechanistic explanation developed to explain this effect of temperature, outlined in Tasks 1.0 and 5.0, supports the speculation that existing loading rate experimental results are sufficient to establish a lower bound temperature response and thus MPT.

The results of these JIP laboratory experiments were analyzed in depth during Phase II research at University of Virginia (UVA), in order to quantify and understand the temperature dependence of IHAC as a function of dissolved hydrogen concentration ^[2], with focus on the implications for establishing an MPT above which IHAC is unlikely. This analysis is summarized in Tasks 1.0 and 5.0 of the ensuing Technical Analysis section and provides the basis for an approach to estimate the MPT necessary to minimize the likelihood of hydrogen embrittlement during pressure vessel shutdown and startup.

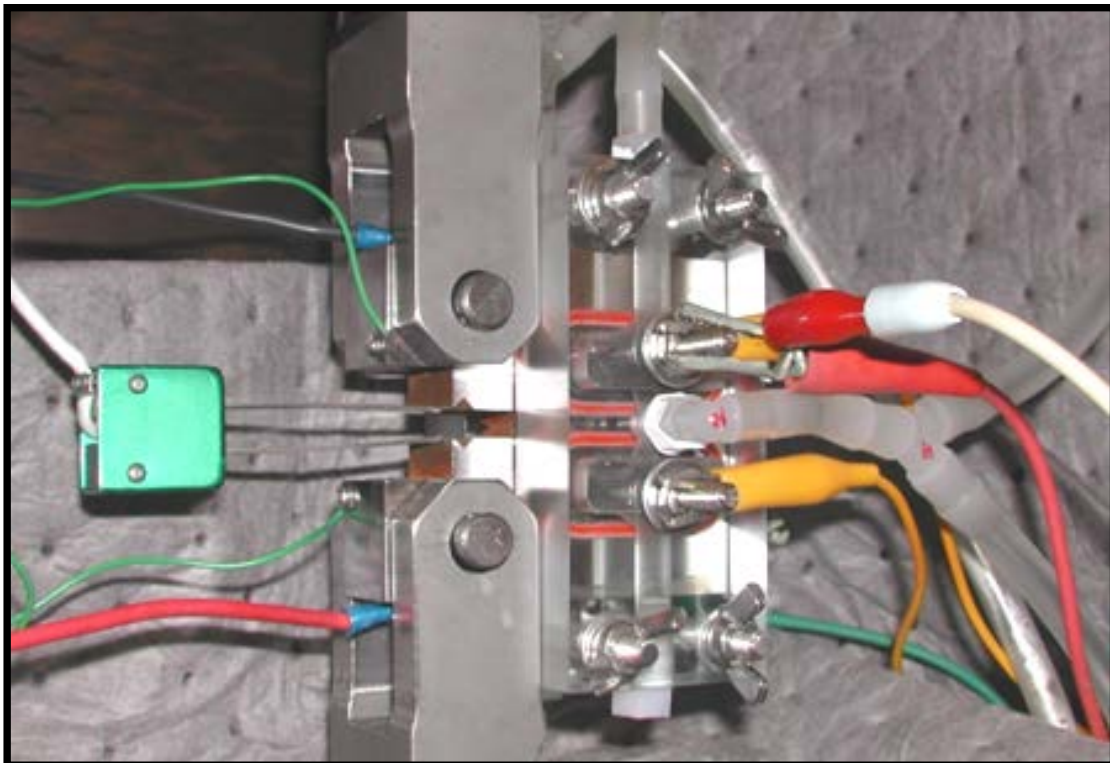
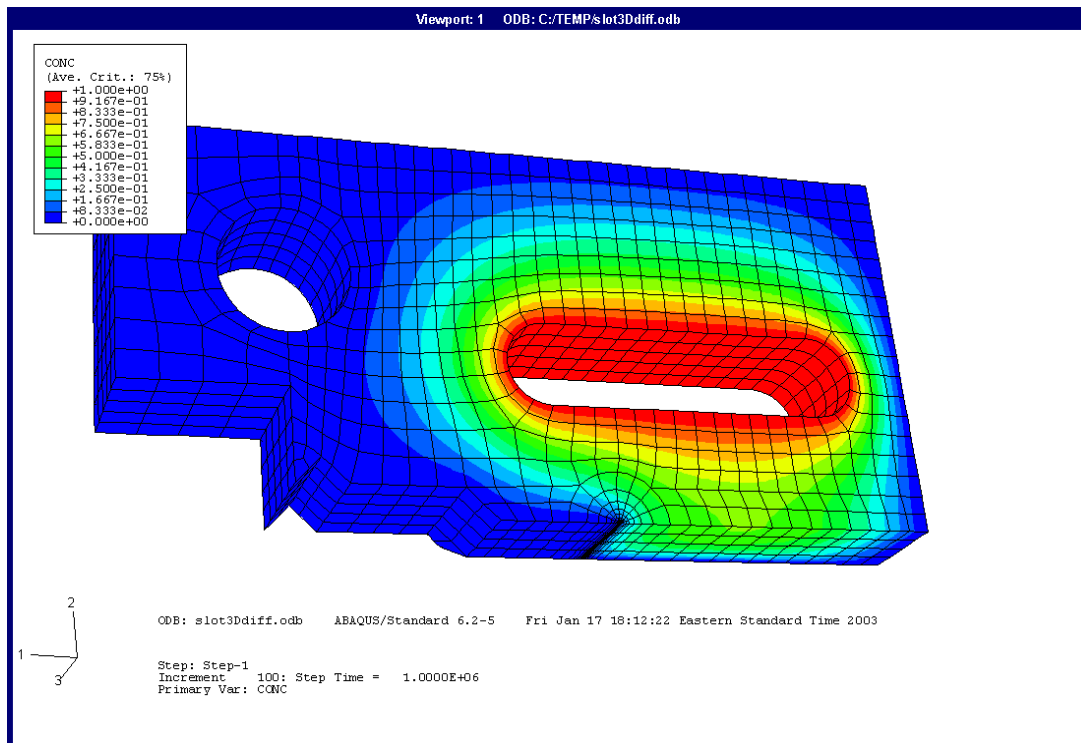


Figure 4—(Top) The slotted compact tension specimen developed in Phase II for laboratory characterization of K_{IH} and da/dt vs K for IHAC without H loss ^[2].

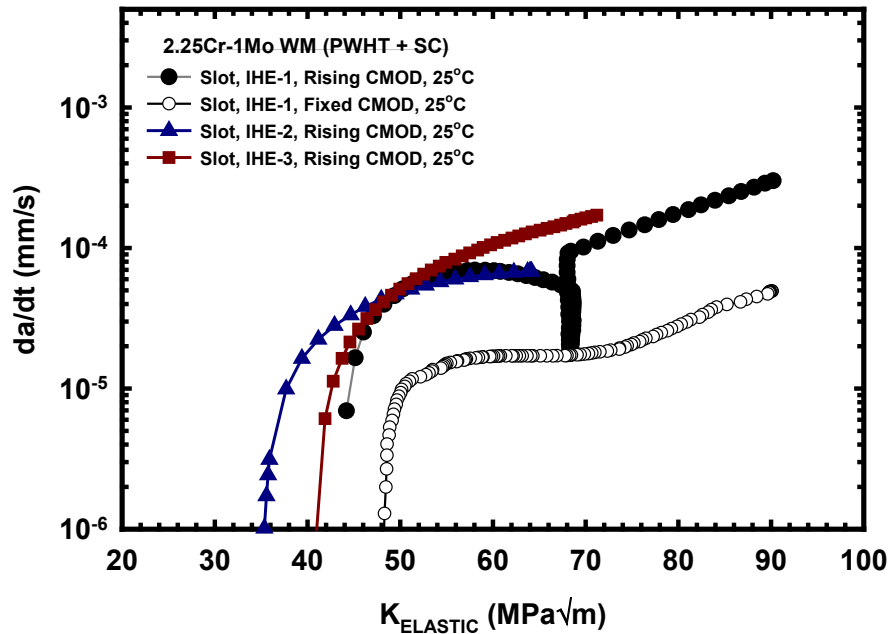


Figure 5—Crack growth rate vs applied stress intensity for the slotted compact tension specimens of 2 $\frac{1}{4}$ Cr-1Mo weld metal stressed under slow-rising CMOD at 25 °C ^[2].

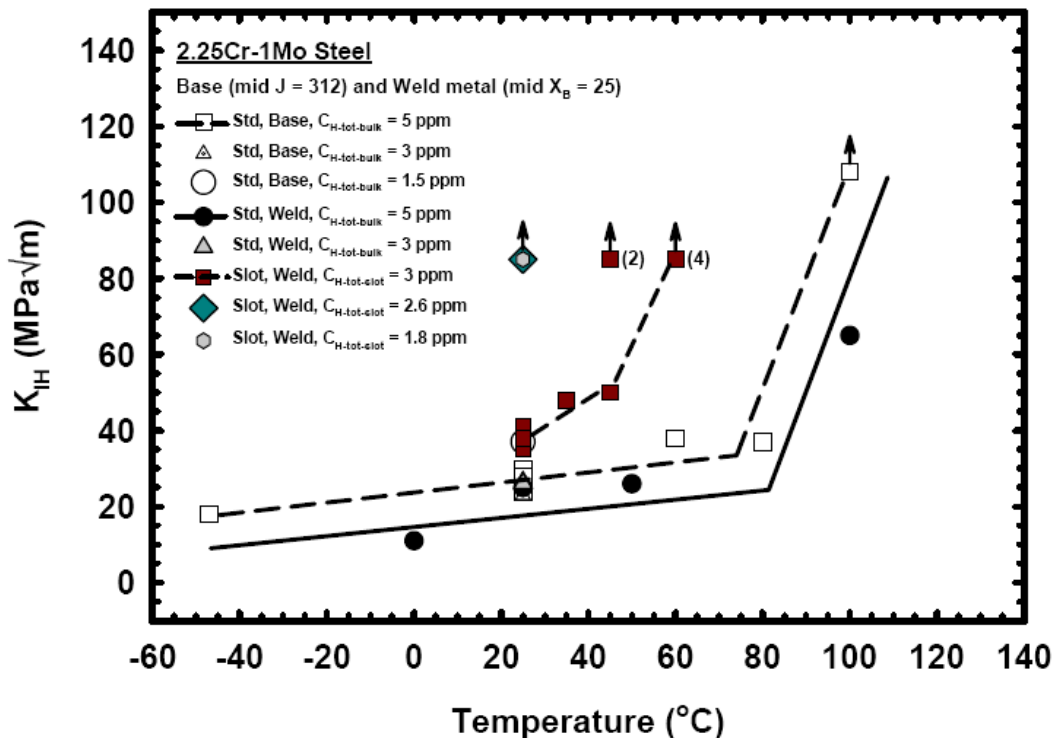


Figure 6—Effect of temperature on the rising CMOD threshold, K_{IH} , for standard H_2 -precharged specimens of 2 $\frac{1}{4}$ Cr-1Mo weld metal from Figure 3, as well as for the slotted compact tension specimen with three levels of electrochemically fixed total H concentration; 3.0 wppm (0.5 M H_2SO_4 + 10^{-3} M K_2SO_4 , -5.0 mA/cm²), 1.8 wppm (0.1 M NaOH, -15 mA/cm²), and 1.1 wppm (0.5 M H_2SO_4 , -10 mA/cm²) on the slot surface ^[2]. [The H concentration listed on the plot for the slotted specimen, 2.6 wppm (♦), is incorrect.]

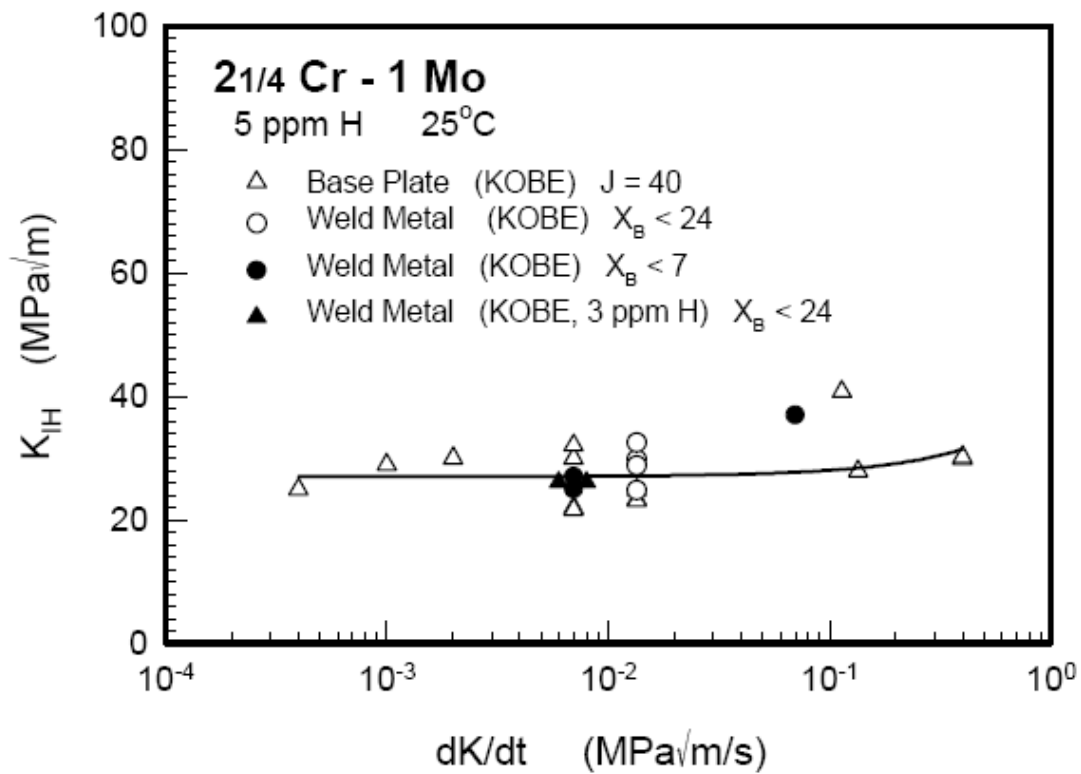


Figure 7—Effect of applied dK/dt , during rising CMOD, on K_{IH} for low-J factor base plate and both low and moderate X_B factor weld metal of 2 1/4Cr-1Mo steel, containing either 5 wppm or 3 wppm of precharged H ($C_{H-Total}$) and stressed at 23 °C^[1].

2 PROBLEM STATEMENT

An API-sponsored committee is working to establish API 934-F, *Guidance on Heavy Wall Reactor Startup and Shutdown*. The strategy is to develop an MPT curve by considering degradation of vessel fracture toughness due to temper embrittlement during service, then to modify the resulting curve to avoid hydrogen-assisted cracking during shutdown and startup. A typical example of the intended engineering guideline, taken from the current draft of this committee document, is illustrated in Figure 8.

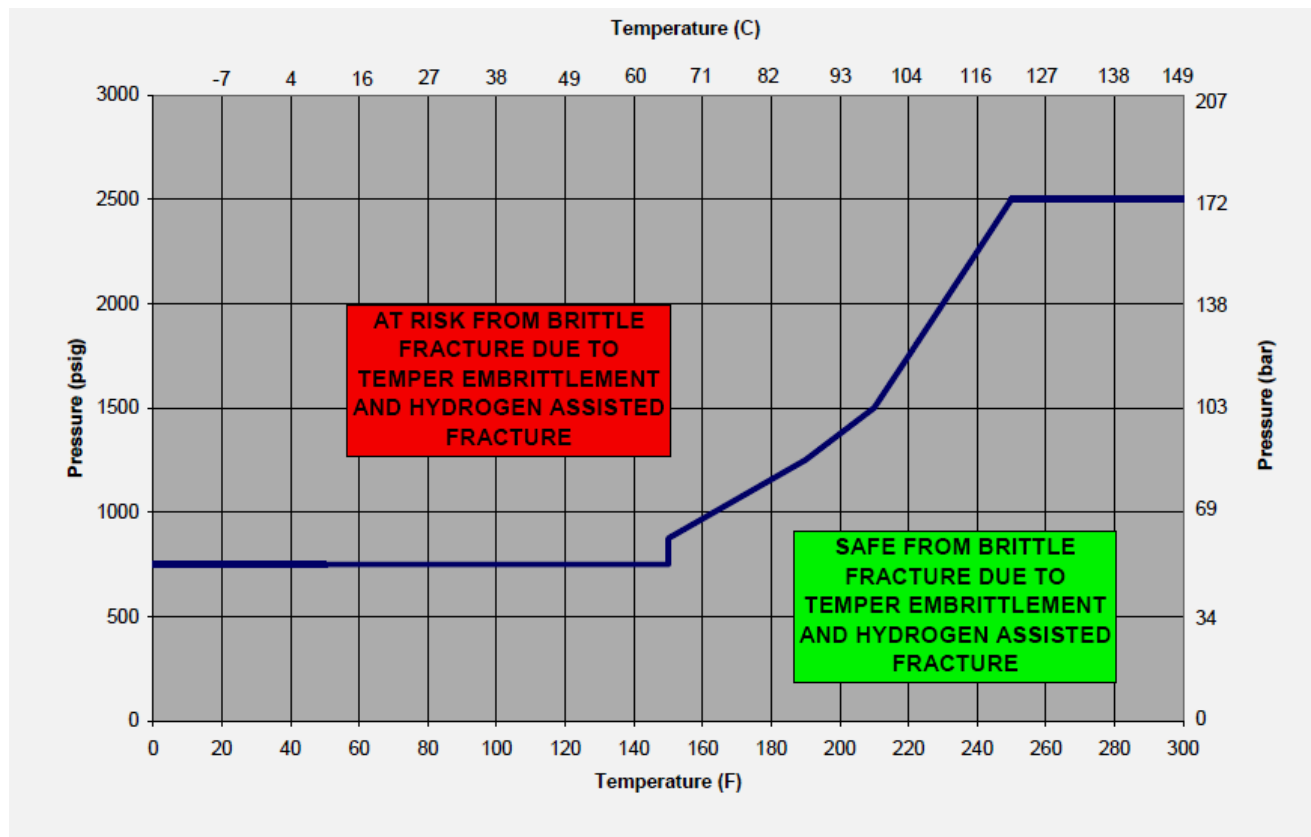


Figure 8—An example of the intended pressurization vs temperature profile for safe-reactor startup, with the MPT of 150 °C established to minimize the likelihood of both catastrophic fracture due to temper embrittlement and subcritical crack propagation due to IHAC.

The temperature-dependent effect of H, predissolved in the thick-wall reactor during elevated-temperature service, on the MPT will depend on steel purity and temper embrittlement history, dissolved H concentration, existing flaw/crack geometry, and loading characteristics during startup or shutdown. This API committee focused on K_{IH} for the onset of subcritical IHAC, typical of the severe rising CMOD laboratory experiments, and selected a plot reported as part of the Phase II data interpretation. The plot is reproduced in Figure 9, where the trend line marked “High Impurity” was reported in Phase II for 2¼Cr-1Mo weld metal of moderate-impurity content ($X_B = 25$ and $J = 276$)¹ and step cooled in the laboratory to promote a single severe degree of temper embrittlement prior to IHAC characterization.

¹ $X_B = (10P + 5Sb + 4Sn + As)100$ in wt %.
 $J = (Si + Mn) (P + X)10^4$ in wt %.

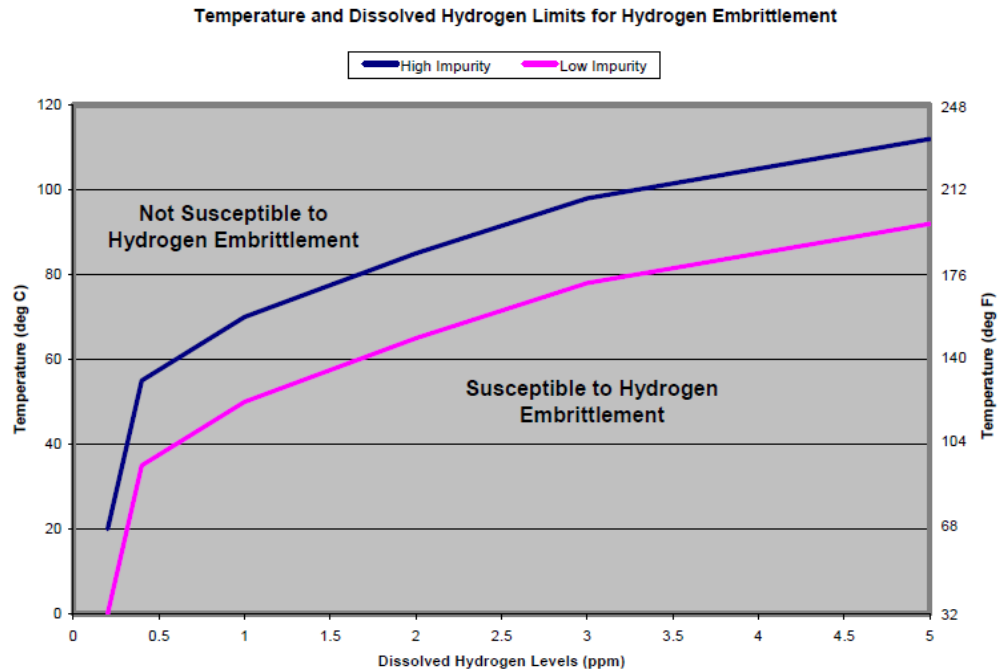


Figure 9—Critical temperature for IHAC vs total dissolved H concentration, predicted specifically for a compact tension specimen fabricated from moderate-purity (“High Impurity”) 2¼Cr-1Mo weld metal [2]. The lower curve for higher-purity 2¼Cr-1Mo steel (“Low Impurity”) is a schematic estimate and not based on specific data or analysis.

The contents of Figure 9 must be applied with caution as several assumptions were made and the result was not intended to be directly relevant to reactor FFS and MPT determination [2]. First, the lower curve, marked “Low Impurity,” was proposed to schematically present the likely effect of improved steel purity and reduced temper embrittlement–IHAC interaction typical of modern higher-purity 2¼Cr-1Mo steel. However, there were no supporting data or quantitative analyses since high-purity modern steels were not considered in the Phase II work. As a second consideration, the assumptions made and mathematical approach taken during the Phase II analysis must be clearly understood as a necessary basis for informed engineering applications of the “Moderate Impurity” MPT trend in Figure 9. For example, this plot in Figure 9 was developed for an idealized compact tension specimen that contained a uniformly dissolved level of H specified on the abscissa, and not a specific detail of a reactor component and existing crack. This fundamentally critical assumption is justified to illustrate the application of PhD research [2], but is unacceptable for quantitative MPT specification.

It is important to:

- a) understand the basis and assumptions used to establish Figure 9, and
- b) generalize this result to include the quantitative effect of steel purity as well as the behavior of a cracked and H-containing reactor detail at the level embodied in REACT.

3 OBJECTIVE AND SCOPE

The objective of this study in support of API 934-F is to document and further develop the technical basis for establishing a MPT necessary to control hydrogen embrittlement of weld metal and base plate of 2¼Cr-1Mo steel used in petrochemical reactor applications. The dependencies of this MPT on dissolved hydrogen concentration and steel purity/temper embrittlement are particularly important to pressure vessel safe operations and will be defined. A secondary objective is to improve the underlying data base for REACT-type fracture mechanics FFS modeling of IHAC.

The approach of this investigation centered on five tasks designed to:

- 1) Summarize and clarify the science-based analysis of H accumulation at the crack tip put forth in Dr. Al-Rumaih's PhD dissertation and confirm the assumptions, input data, and modeling results used in this Phase II JIP research ^[2]. The aim of this work, centered on moderate-impurity 2¼Cr-1Mo steel, is to quantitatively establish the H concentration–temperature dependence of the threshold for IHAC in Phase I standard laboratory specimens (K_{IH}), as a foundation to predict MPT and conduct fitness-for-hydrogen-service analyses.
- 2) Validate the Phase II correlation of K_{IH} and critical temperature vs H concentration based on new analysis of post-Phase-II laboratory data obtained to describe IHAC of moderate-purity 2¼Cr-1Mo steel using ultra-thick compact tension specimens.
- 3) Enhance the Phase II analysis of K_{IH} vs crack tip H concentration, and thus MPT, by describing the interaction between temper embrittlement and IHAC using JIP Phase I data so as to predict the influence of modern steel purity.
- 4) Build on the hydrogen-damage-mechanism-based master correlation between K_{IH} and crack tip stress field/microstructure-trapped H to develop a H concentration similitude parameter that is useful in engineering analysis of thick-wall reactor FFS and MPT.
- 5) Validate the empirically based trends and predictions of the effects of temperature and steel purity on the threshold stress intensity through consideration of the state-of-the art theory and micromechanical modeling of IHAC.

This analysis is limited to a K_{IH} -based approach to describe the onset of subcritical IHAC. In this context the MPT is based on the steel temperature above which K_{IH} for a given bulk H concentration approaches K_{IC} for hydrogen-free steel. Prediction of subcritical IHAC damage accumulation, and residual vessel life, based on crack growth rates and crack extension at temperatures below the MPT, is not considered. Possible enhancement of unstable or tearing fracture due to dissolved H is not considered. The former assumption is dictated by the complexity of a crack-growth-rate-based inspection interval approach, best considered after a K_{IH} -based MPT strategy is developed. The latter assumption is justified base on the limited and weak data base, as well as fundamental understanding, for H reduction of K_{IC} to K_{IC-H} as well as reduced R-curve resistance to stable tearing.

4 ACRONYMS AND ABBREVIATIONS

For the purposes of this document, the following definitions apply.

1-D	one-dimensional
2-D	two-dimensional
3-D	three-dimensional

AB	Anderson–Brown
AG	Al-Rumaih–Gangloff
CMOD	crack mouth opening displacement
FATT	fracture appearance transition temperature
FEA	finite element analysis
FFS	fitness-for-service
FPZ	fracture process zone
HEAC	hydrogen environment assisted cracking
IHAC	internal hydrogen-assisted cracking
JIP	joint industry program
MPT	minimum pressurization temperature
UVa	University of Virginia

5 TECHNICAL ANALYSIS

Task 1.0—Summarize and clarify the technical approach, assumptions, data, and modeling results used in Phase II JIP research to quantitatively establish the H concentration and temperature dependencies of the threshold stress intensity, K_{IH} , for IHAC and the concentration dependence of MPT for moderate-impurity 2½Cr-1Mo steel.

The approach to modeling the temperature and dissolved hydrogen concentration dependencies of K_{IH} for IHAC, and the role of such cracking in determining an MPT vs hydrogen concentration, was detailed in Phase II and developed in the PhD research of Abdullah Al-Rumaih, who provided important inputs to the development of this Task 1.0 report ^[2]. This contribution is acknowledged.

The approach is based on the following three concepts.

- 1) A master correlation can be developed between measured K_{IH} and the concentration of embrittling H enriched at a single reference point near to the crack tip where H damage is likely. This relationship should be independent of the source of the hydrogen, be it uniform precharging in high-temperature, high-pressure H₂ or active slot, electrochemical charging of a laboratory specimen, as well as in-service charging of a stainless steel clad pressure vessel ID.
- 2) The role of temperature in IHAC centers on the extent to which thermal energy promotes H escape from those trap sites that constitute a connected crack path through the steel microstructure. Simply stated, K_{IH} will increase with increasing temperature because of decreasing concentration of H that is locally enriched (i.e. trapped) along the brittle crack path.
- 3) The master correlation between K_{IH} and crack tip H concentration will depend on steel metallurgy, particularly purity and the degree of temper embrittlement developed during elevated-temperature service.

A unique K_{IH} correlation is based on a H concentration similitude parameter, as detailed in Task 4.0 and that relates laboratory data on IHAC to component performance in hydrogen service. This concept parallels well-accepted fracture mechanics similitude, considered in the context of the three regions of crack tip mechanics that are relevant to IHAC.

- 1) The crack tip fracture process zone (FPZ), within which normal and hydrostatic stresses (σ_H) are substantially enhanced [with the latter equaling between 2.5 and 10 times the uniaxial yield strength (σ_{YS})] is immediately proximate to the crack tip surface, extending inward by a length approximated by twice the blunted crack tip opening displacement, CTOD, given by:

$$\delta_{FPZ} = \frac{2 d_n K^2}{\sigma_{YS} E}$$

where d_n is a material constant determined from elastic-plastic fracture mechanics and taken as 0.5 for the Phase II analysis. Hydrogen concentration is greatly enhanced and thus IHAC damage is localized strictly within this zone. As such, it is the concentration of embrittling H present at this location that is relevant to K_{IH} and is provided by mass transport through Zones 2) and 3) described below.

- 2) The FPZ is contained within the crack tip plastic zone of diameter (r_P), which is approximated by the well-known relationship for plane strain crack tip plasticity:

$$r_P = \frac{2}{17.3\pi} \left(\frac{K}{\sigma_{YS}} \right)^2$$

The size of this zone is not fundamentally relevant to IHAC or modeling, but may affect H diffusion to Zone 1) and affects the level of concentrated stresses in the Zone 1) FPZ.

- 3) The crack tip plastic zone is contained within the larger regime where elastic stresses are elevated by the relationship between K and inverse square root distance from the crack tip. This aspect of the crack tip field provides the foundation for macroscopic modeling of pressure vessel FFS through K similitude used in REACT.

For the Cr-Mo base plates and weld metals of interest—where in general $E = 200,000$ MPa, $\sigma_{YS} = 500$ MPa, $1/n = 0.65$, and K_{IH} for IHAC = 20 to 80 MPa $\sqrt{m}$ — $\delta_{FPZ} = 5$ to 85 μm and $r_P = 60$ to 960 μm , depending on the level of applied K .

The central hypothesis is that K_{IH} is a unique function of the concentration of H trapped along the observed crack path and specifically located at δ_{FPZ} where normal stresses are highest to interact with this H concentration to drive IHAC. Gradients of H concentration, hydrostatic stress, and temperature, as well as the diffusivity of H in trap-rich Cr-Mo microstructure, govern the amount of lattice H present at this near-crack tip location after exposure to a given time–temperature history. This lattice H is enhanced by hydrostatic stress, during loading, plus H-trap binding energy specific to crack path damage sites. In Phase II Al-Rumaih developed this correlation for the H content localized in the crack tip FPZ, very close ($\delta_{FPZ} \sim 10$ μm) to the crack tip. This location required a complex H diffusion and trapping analysis that is summarized below for moderate-purity temper embrittled Cr-Mo base plate and weld metal. Subsequent sections of this report will add new laboratory IHAC data to this correlation and will consider alternate locations for the H enrichment similitude parameter, selected to simplify the diffusion analysis. The governing concentration of crack-tip-enriched H within δ_{FPZ} , $C_{T\sigma}$, is given by:

$$C_{T\sigma} = C_L \exp \left(\frac{\sigma_H V_H + E_B}{RT} \right)$$

where C_L is the concentration of H present in lattice sites at δ_{FPZ} in the FPZ defined by the location of highest hydrostatic tension (σ_H), V_H is the partial molar volume of H in iron, R and T have the normal meaning, and

E_B is the binding energy of H to the traps sites that constitute the crack path. For the Cr-Mo steel weld metal considered in Phase II, this crack path follows bainite lath and packet boundaries plus prior austenite grain boundaries [2]. There are three uncertainties associated with this equation: specifically, the correct values of C_L for a given bulk level of dissolved H, as well as values of σ_H and E_B for a strained crack tip and complex-steel microstructure; each has been the object of substantial literature debate.²

Using reasonable assumptions, it is possible to estimate $C_{T\sigma}$ for several laboratory data sets relevant to IHAC of Cr-Mo steel, including H provided to the crack tip from either high-temperature H₂ precharging of a standard compact tension specimen or the electrochemical slot case shown in Figure 4. This was accomplished in the Phase II work [2], and key results are presented in Figures 10 and 11 for two likely bounding values of E_B : 38 kJ/mol for H trapped at bainite interfaces and 59 kJ/mol for H trapped at prior austenite grain boundaries. For each case, there is a clear correlation between decreasing measured K_{IH} and increasing calculated $C_{T\sigma}$ at δ_{FPZ} , capturing the beneficial effect of increasing temperature.

² In IHAC analysis, the various forms of total, trapped, and lattice-soluble H concentrations can create confusion. The total H present in a complex steel microstructure ($C_{H-Total}$) is the sum of diffusible (C_{H-Diff}) and deeply trapped immobile H. The C_{H-Diff} is the sum of H dissolved in lattice sites (C_L) plus the H concentration associated with reversible traps that are largely dislocations and fine-scale carbides in the bainitic microstructure of 2¼Cr-1Mo steel. During elevated-temperature exposure to H₂, $C_{H-Total} = C_L$ since H trapping does not occur due to high thermal energy that exceeds the H-trap binding energy, E_B . This $C_{H-Total}$ is measured by LECO-type hot extraction at 600 °C of specimens that are “quenched” to ambient to retain all H; this $C_{H-Total}$ is typically cited in experimentally determined Sievert’s Law solubility relationships. However, $C_{H-Total}$ should not be used in a H diffusion analysis in the temperature range where H trapping occurs. The C_{H-Diff} represents mobile H relevant to diffusion modeling, but the precise definition of the boundary between reversible and deep-irreversible trap sites is vague. Reversibly trapped H exchanges, at equilibrium, between H dissolved in the surrounding lattice and that on the trap site, with equal rates of trapping and escape. This diffusible H is governed by trapping and detrapping rates and is measured by low-temperature permeation and ambient temperature outgassing experiments. This diffusible H concentration and mobile H diffusivity depend sensitively on trap binding energy and density in the microstructure. For the Cr-Mo weld metal studied in Phase II, experiments showed that C_{H-Diff} at 25 °C equaled 65 % of $C_{H-Total}$. In this context, the mobility of diffusible H is reasonably described by an effective H diffusivity, D_{Eff} , that is less than the H diffusivity, D_L , for the Fe-Cr-Mo lattice. It is well known that:

$$\frac{C_{H-Diff}}{C_L} \approx \frac{D_L}{D_{Eff}}$$

For the Phase II weld metal, D_{Eff} is 1×10^{-6} cm²/s, but decreases with decreasing mobile H concentration and increasing plastic strain (dislocation trap density) typical of the crack tip region [2]. Since D_L for pure Fe is about 1×10^{-5} cm²/s, this relationship suggests that $C_L = 0.1 C_{H-Diff}$. D_L for the Fe-Cr-Mo matrix is uncertain, but comparison between the literature value of C_L for pure iron in H₂SO₄ and measured C_{H-Diff} for the Phase II Cr-Mo weld metal at the same applied cathodic overpotential also shows that $C_L = 0.1 C_{H-Diff}$. However, counter to this good agreement, it is believed that those fine carbides that control D_{Eff} are characterized by a H-trap binding energy of $E_B = 11.5$ kJ/mol [2]. This trap strength corresponds to a C_{H-Diff} of 100 C_L , rather than the value of 10 C_L used by Al-Rumaih in his Phase II correlation [2]. As a final caution, the proportionality constant between lattice and diffusible H concentrations may vary with temperature and Cr-Mo microstructure; these complications were not modeled in Phase II. The bottom line for the present analysis is that both analytical and finite element modeling of H diffusion should employ D_{Eff} and C_{H-Diff} , both of which depend on H trapping. In MPT analysis, it is particularly important to maintain consistency in these terms and to clearly state the type of H concentration that is predicted, be it $C_{H-Total}$ in equilibrium with high-temperature H₂ or C_{H-Diff} that can migrate to a crack tip stress field during loading.

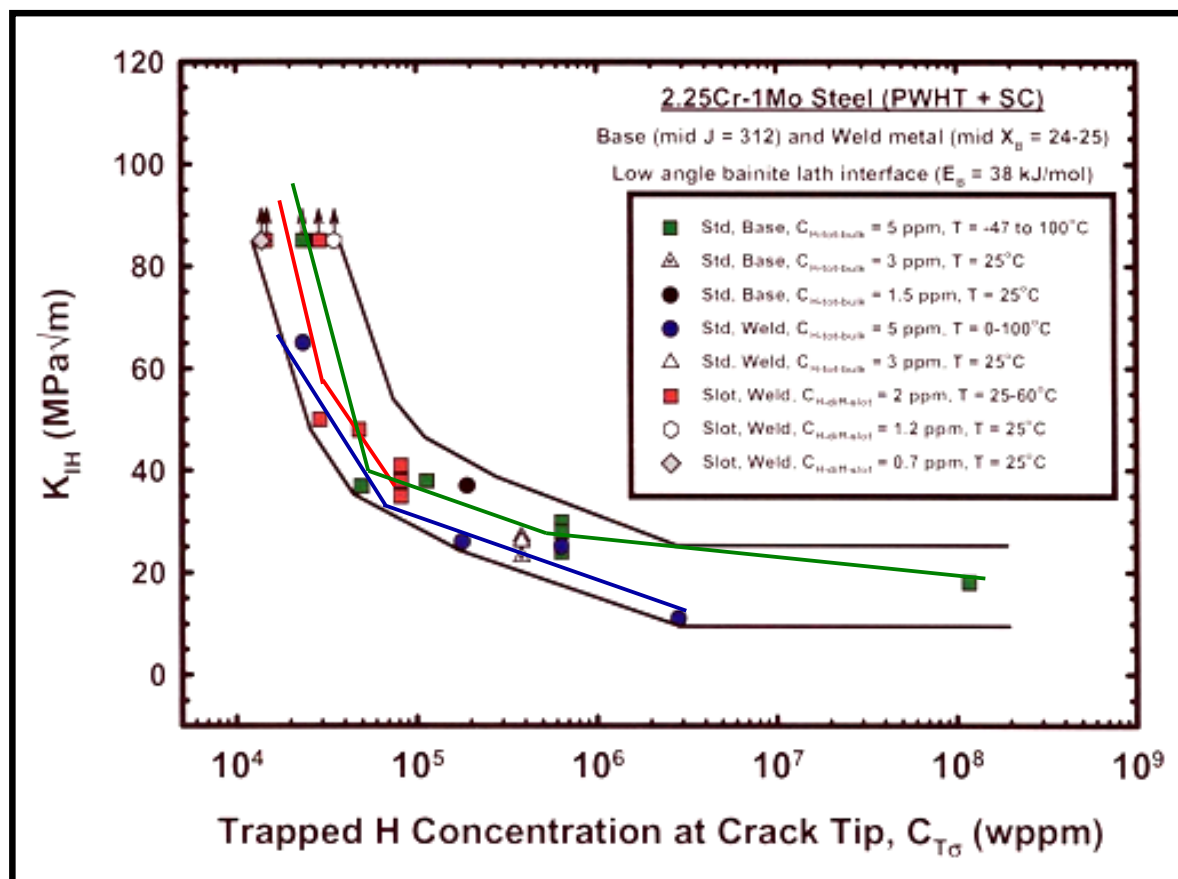


Figure 10—Correlation between measured K_{IH} vs model-predicted concentration of H, trapped along the crack path with a binding energy, E_B , of 38 kJ/mol and in the crack tip hydrostatic stress field, at a reference distance of $\delta_{FPZ} = 9 \mu\text{m}$ ahead of the tip for moderate-purity 2½Cr-1Mo base plate and weld metal subjected to laboratory step cooling to promote a typical level of temper embrittlement [2]. Charpy impact fracture appearance transition temperature (FATT) values are 6 °C for the base plate and 28 °C to 43 °C for the weld metal, as amplified in the text. In the figure legend, $C_{H\text{-Total Bulk}}$ is listed for standard H_2 -precharged compact tension specimens, and $C_{H\text{-Diff Slot}}$ is listed for slotted compact tension specimens charged from each of the three electrolytes noted in Figure 6. $C_{T\sigma}$ was calculated using σ_{YS} of 500 MPa for weld metal and 465 MPa for base plate. The 3-D diffusion model included $D_{H\text{-Eff}}$ that depended on $C_{H\text{-Diff}}$, temperature, and plastic strain for $K = 0 \text{ MPa}\sqrt{\text{m}}$. Since $K = 0$, the diffusion model estimated H redistribution from the starting condition during specimen setup, without loading, but did not include the estimated effect of subsequent dK/dt on H redistribution to the crack tip damage location at δ_{FPZ} .