

The Effects of Hydrogen for Establishing a Minimum Pressurization Temperature (MPT) for Heavy Wall Steel Reactor Vessels

API TECHNICAL REPORT 934-F, PART 4
FIRST EDITION, NOVEMBER 2018



AMERICAN PETROLEUM INSTITUTE

The Effects of Hydrogen for Establishing a Minimum Pressurization Temperature (MPT) for Heavy Wall Steel Reactor Vessels

Prepared under contract for API by:

Dr. Richard P. Gangloff
Emeritus Ferman W. Perry Professor of Materials Science and Engineering
Department of Materials Science and Engineering
School of Engineering and Applied Science
University of Virginia, Charlottesville, Virginia

Ted L. Anderson, Ph.D., P.E.
TL Anderson Consulting
Longmont, Colorado



AMERICAN PETROLEUM INSTITUTE

Special Notes

API publications necessarily address problems of a general nature. With respect to particular circumstances, local, state, and federal laws and regulations should be reviewed.

Neither API nor any of API's employees, subcontractors, consultants, committees, or other assignees make any warranty or representation, either express or implied, with respect to the accuracy, completeness, or usefulness of the information contained herein, or assume any liability or responsibility for any use, or the results of such use, of any information or process disclosed in this publication. Neither API nor any of API's employees, subcontractors, consultants, or other assignees represent that use of this publication would not infringe upon privately owned rights.

Classified areas may vary depending on the location, conditions, equipment, and substances involved in any given situation. Users of this technical report should consult with the appropriate authorities having jurisdiction.

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to assure the accuracy and reliability of the data contained in them; however, the Institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any authorities having jurisdiction with which this publication may conflict.

API publications are published to facilitate the broad availability of proven, sound engineering and operating practices. These publications are not intended to obviate the need for applying sound engineering judgment regarding when and where these publications should be utilized. The formulation and publication of API publications is not intended in any way to inhibit anyone from using any other practices.

Any manufacturer marking equipment or materials in conformance with the marking requirements of an API standard is solely responsible for complying with all the applicable requirements of that standard. API does not represent, warrant, or guarantee that such products do in fact conform to the applicable API standard.

Users of this technical report should not rely exclusively on the information contained in this document. Sound business, scientific, engineering, and safety judgment should be used in employing the information contained herein.

Where applicable, authorities having jurisdiction should be consulted.

API is not undertaking to meet the duties of employers, manufacturers, or suppliers to warn and properly train and equip their employees, and others exposed, concerning health and safety risks and precautions, nor undertaking their obligations to comply with authorities having jurisdiction.

All rights reserved. No part of this work may be reproduced, translated, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the Publisher, API Publishing Services, 1220 L Street, NW, Washington, DC 20005.

Copyright © 2018 American Petroleum Institute

Foreword

Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

Questions concerning the interpretation of the content of this publication or comments and questions concerning the procedures under which this publication was developed should be directed in writing to the Director of Standards, American Petroleum Institute, 1220 L Street, NW, Washington, DC 20005. Requests for permission to reproduce or translate all or any part of the material published herein should also be addressed to the director.

Generally, API standards are reviewed and revised, reaffirmed, or withdrawn at least every five years. A one-time extension of up to two years may be added to this review cycle. Status of the publication can be ascertained from the API Standards Department, telephone (202) 682-8000. A catalog of API publications and materials is published annually by API, 1220 L Street, NW, Washington, DC 20005.

Suggested revisions are invited and should be submitted to the Standards Department, API, 1220 L Street, NW, Washington, DC 20005, standards@api.org.

Contents

	Page
1 Executive Summary	1
2 Introduction	2
3 Critical Review of Experimental Data for Hydrogen Effects On 2 ¼ Cr-1 Mo Steel	3
3.1 Background	3
3.2 Subcritical Hydrogen Cracking Threshold Stress Intensity (K_{IH})	16
3.3 Resistance to Fast Fracture in Hydrogen Charged Steels (K_{IC-H})	28
3.4 Internal Hydrogen Assisted Cracking of Modern 2¼Cr-1Mo-0.25V	58
3.5 Hydrogen Environment Assisted Cracking of Cr-Mo and Cr-Mo-V Steels	61
3.6 References	63
4 Technical Basis for an MPT Determination	68
4.1 Critical Temperature for Subcritical Hydrogen Cracking	68
4.2 Pressure-Temperature Curve for Fast Fracture Avoidance	79
4.3 References	84
5 Proposed Architecture for a Fitness-for-Service Procedure	86
5.1 FATT Estimation	86
5.2 Critical Temperature for Stable Hydrogen Cracking (T_{IH})	88
5.3 Fast Fracture Avoidance	97
6 Conclusions	97

Figures

1 Schematic diagram of the effect of loading format on the IHAC and HEAC of low-alloy Cr-Mo steels, noting the material properties relevant to fracture mechanics assessment of minimum pressurization temperature and fitness-for-service	4
2 The ultimate tensile strength dependence of the threshold stress intensity for the onset of IHAC under slow-rising CMOD loading (K_{IH}) compared to the arrest of IHAC under fixed-CMOD (K_{TH} under decreasing K) loading for H-precharged 2¼Cr-1Mo steel stressed at 25 °C	6
3 Historical record of improving 2¼Cr-1Mo purity	13
4 Relationship between $FATT_{Thermal}$ and J for Cr-Mo steels subjected to long-term in-service exposure showing the occurrence of temper embrittlement	14
5 Effect of loading format on IHAC for low-J base plate of 2.48%Cr-1.10%Mo ($J = 40$, $FATT_{Thermal}$ after step cool = -90°C, $\sigma_{YS} = 447$ MPa), precharged with a total-H concentration of 5.7 wppm, then stressed in moist air under slow-rising CMOD ($dK/dt = 0.007$ MPa√m/s) at 25 °C	19
6 Effect of loading rate on K_{IH} for the low-J base plate in Figure 5, plus data for low X_B weld metal (step cooled $FATT_{Thermal} = -57^\circ\text{C}$) and moderate X_B weld metal (step cooled $FATT_{Thermal} = 32^\circ\text{C}$) with the indicated predissolved total H concentration	20
7 Effect of loading rate on the da/dt during rising CMOD, at K midway between K_{IH} and the highest K in the loading, for the base plate, two weld metals, and H concentrations shown in Figure 6	21
8 Effect of total-dissolved H concentration, produced by elevated temperature exposure in high-pressure H_2 , on the elastic K_{IH} for high-purity (low J and X_B) weld metal and base plate of 2¼Cr-1Mo stressed in moist air at a single-slow-rising CMOD and 23 °C	22

Contents

Page

9	Effect of total-dissolved H concentration, produced by elevated temperature exposure in high-pressure H ₂ , on the elastic K _{IH} for moderate purity (mid J and X _B) weld metal (step cooled FATT _{Thermal} = 28 °C and 45 °C) and base plate (step cooled FATT _{Thermal} = 6 °C) of 2¼Cr-1Mo stressed in moist air at a single-slow-rising CMOD rate and 23 °C	23
10	Effect of total-dissolved H concentration, produced by elevated temperature exposure in high-pressure H ₂ , on the elastic K _{IH} for low-purity (high J and X _B) weld metals and base plates of 2¼Cr-1Mo stressed in moist air at a slow-rising CMOD (0.005 MPa√m/s to 0.135 MPa√m/s) and 23 °C	24
11	Effect of temperature on the elastic K _{IH} for H ₂ -precharged (initial value of C _{H-Total} = 5 wppm) moderate-purity weld metal and base plate of 2¼Cr-1Mo stressed in moist air at a slow-rising CMOD (0.007 MPa√m/s)	26
12	Effect of temperature on the rising-CMOD threshold, K _{IH} , for standard H ₂ -precharged specimens of 2¼Cr-1Mo weld metal from Figure 11, as well as for the slotted compact tension specimen with three levels of total H concentration, electrochemically fixed on the slot surface; C _{H-Total} = 3.0 wppm (0.5 M H ₂ SO ₄ + 10 ⁻³ M K ₂ SO ₄ at -5.0 mA/cm ²), C _{H-Total} = 1.8 wppm (0.1 M NaOH at -15 mA/cm ²), and C _{H-Total} = 1.1 wppm (0.5 M H ₂ SO ₄ at -10 mA/cm ²)	27
13	Effect of temperature on the rising-CMOD threshold, K _{IH} , for 90-mm-thick compact tension specimens of H ₂ -precharged specimens of moderate FATT _{Thermal} 2¼Cr-1Mo weld metal and base plate	28
14	Left: Effect of predissolved H concentration on the difference in the FATT, with and without H, for 2¼Cr-1Mo with and without temper embrittlement from step cooling. Right: Effect of predissolved H and temper embrittlement from step cooling on the Charpy FATT for several compositions of Cr-Mo steel	30
15	Effect of H concentration on the increase in FATT, per 1.0 wppm of predissolved H, for base metal, weld metal, and the HAZ 2¼Cr-1Mo steel	31
16	Hydrogen distribution among lattice (L) and trap sites [(a): carbide (C) interfaces, lath interfaces, grain boundaries (GB), and dislocations (D), and (b): lath interfaces (Lath)] during cooling of H-precharged 2¼Cr-1Mo from the charging temperature	32
17	Master curve correlation of H-free fracture toughness, K _{IC} , (open diamonds) for Cr-Mo steels of varying FATT and without	36
18	The effect of loading temperature on the critical stress intensity for the onset of crack propagation in a Cr-Mo steel	38
19	The effect of loading temperature on the critical stress intensity for the onset of crack propagation in a Cr-Mo steel	39
20	The effect of H on crack growth resistance under rising CMOD loading at 100 °C	40
21	The predicted dependence of the H-induced shift in transition temperature as a function of steel FATT, in the temper embrittled condition, and C _{H-Total}	42
22	The relationship between H-free FATT _{Thermal} and the FATT _{Thermal} after H precharging to a C _{H-Total} of 2 wppm for various heats of 2¼Cr-1Mo steel	43
23	The predicted operating pressure-temperature profile necessary to avoid H cracking during thick wall reactor startup	44
24	The effect of loading, given by K _{Elastic} , on the magnitude of the plastic part of K calculated from the J-integral based on unloading compliance for 25.4-mm-thick CT specimens of 2¼Cr-1Mo with crack lengths and load levels typical of IHAC experiments	47
25	The effect of loading temperature on the occurrence (y-axis value near +1.0) or absence (y-axis value near -1.0) of unstable H cracking in 2¼Cr-1Mo base plate of varying temper embrittled FATT _{Thermal} between -90 °C and +130 °C, and with an average-precharged C _{H-Total} of between 1.1 wppm and 5.5 wppm. y-axis values ≈ -1.8 indicate those experiments where the applied K was less than 60 MPa√m	50

Contents

Page

26	The effect of $(T - FATT_{Thermal})$ on the occurrence (y-axis value $\approx +1.0$) or absence (y-axis value ≈ -1.0) of unstable-H cracking in 2¼Cr-1Mo base plate of varying temper embrittled $FATT_{Thermal}$ between -90°C and $+130^{\circ}\text{C}$, and with an average precharged $C_{H-Total}$ of between 1.1 wppm and 5.5 wppm. y-axis values ≈ -1.8 indicate those experiments where the applied K was less than $60 \text{ MPa}\sqrt{\text{m}}$	51
27	The effect of loading temperature on the occurrence (y-axis value $\approx +1.0$) or absence (y-axis value ≈ -1.0) of unstable H cracking in 2¼Cr-1Mo weld metal of varying temper embrittled $FATT_{Thermal}$ between -57°C and $+88^{\circ}\text{C}$, and with an average-precharged $C_{H-Total}$ of between 1.9 wppm and 5.9 wppm. y-axis values ≈ -1.8 indicate those experiments where the applied K was less than $60 \text{ MPa}\sqrt{\text{m}}$	55
28	The effect of $(T - FATT_{Thermal})$ on the occurrence (y-axis value $\approx +1.0$) or absence (y-axis value ≈ -1.0) of unstable-H cracking in 2¼Cr-1Mo weld metal of varying temper embrittled $FATT_{Thermal}$ between -57°C and $+88^{\circ}\text{C}$, and with an average-precharged $C_{H-Total}$ of between 1.9 wppm and 5.9 wppm. y-axis values ≈ -1.8 indicate those experiments where the applied K was less than $60 \text{ MPa}\sqrt{\text{m}}$	56
29	The effect of loading temperature on the occurrence (y-axis value $\approx +1.0$) or absence (y-axis value ≈ -1.0) of unstable-H cracking in 2¼Cr-1Mo base plate and weld metal of varying temper embrittled $FATT_{Thermal}$ between -90°C and $+130^{\circ}\text{C}$, and with an average-precharged $C_{H-Total}$ of between 1.1 wppm and 5.9 wppm. y-axis values ≈ -1.8 indicate those experiments where the applied K was less than $60 \text{ MPa}\sqrt{\text{m}}$	57
30	The effect of $(T - FATT_{Thermal})$ on the occurrence (y-axis value $\approx +1.0$) or absence (y-axis value ≈ -1.0) of unstable-H cracking in 2¼Cr-1Mo base plate and weld metal of varying temper embrittled $FATT_{Thermal}$ between -90°C and $+130^{\circ}\text{C}$, and with an average-precharged $C_{H-Total}$ of between 1.1 wppm and 5.9 wppm. y-axis values ≈ -1.8 indicate those experiments where the applied K was less than $60 \text{ MPa}\sqrt{\text{m}}$	58
31	The loading rate dependence of K_{IH} for IHAC in 2¼Cr-1Mo-0.25V base metal (BM, $\blacktriangle$) and weld metal (WM, $\triangle$) at 25°C compared to values for 2¼Cr-1Mo BM and WM at 25°C (Figure 6) using the conservative slow-rising CMOD test method used in the Phase I JIP	59
32	The temperature dependence of K_{IH} for IHAC in 2¼Cr-1Mo base metal and weld metal from Figure 11, compared to K_{IH} for 2¼Cr-1Mo-0.25V BM and WM for slow rising dK/dt that generally increased with increasing temperature	60
33	The $C_{H-Total}$ dependence of K_{IH} for IHAC in modern low J-factor 2¼Cr-1Mo BM and WM, replotted from Figure 8 and compared to that for 2¼Cr-1Mo-0.25V weld and base metals.	61
34	The H_2 pressure dependence of the threshold stress intensity for HEAC of alloy and C-Mn steels stressed at 25°C	62
35	H_2 pressure dependence of K_{IH} for slow-rising K stressing of as-received and H-precharged 2¼Cr-1Mo-0.25V base metal and weld metal in pure H_2	63
36	Correlation between measured K_{IH} and the 3-D finite element model-predicted concentration of H, trapped along the crack path with an E_B of 38 kJ/mol at a reference distance ($\delta_{9\mu\text{m}}$) of $9 \mu\text{m}$ ahead of the tip for moderate-purity laboratory step-cooled 2¼Cr-1Mo base plate and weld metal .	70
37	The effect of crack tip diffusible H concentration ($C_{H-Diff 470 \mu\text{m}}$), localized at the reference point of $\delta_{470 \mu\text{m}}$ ahead of the crack tip, on the predicted critical temperature for elimination of IHAC in a cracked section fabricated from moderate- $FATT_{Thermal}$ 2¼Cr-1Mo steel (Database B, Section 3.1.5), as a function of total-precharged H concentration and based on the laboratory value of $C_{T\sigma-CRIT} = 117,000 \text{ wppm}$ taken from Figure 36 and enhanced to account for the increase in crack tip reference location from $9 \mu\text{m}$ to $470 \mu\text{m}$	71
38	K_{IH} master curve for Low- $FATT$ (Database C, $FATT_{Thermal} < -30^{\circ}\text{C}$) 2¼Cr-1Mo base plate and weld metal	74

Contents

	Page
39 K_{IH} master curve for Medium-FATT (Database B, $-30\text{ }^{\circ}\text{C} < \text{FATT}_{\text{Thermal}} < 50\text{ }^{\circ}\text{C}$) 2¼Cr-1Mo base plate and weld metal	75
40 K_{IH} master curve for High-FATT (Database A, $\text{FATT}_{\text{Thermal}} > 50\text{ }^{\circ}\text{C}$) 2¼Cr-1Mo base plate and weld metal	75
41 Through-wall variation of hydrogen content at steady-state operating conditions (blue curve) and during a shutdown transient (red curve).	76
42 Using the Φ parameter to ensure similitude between a laboratory specimen and a reactor with a surface crack	78
43 Critical temperature versus bulk hydrogen content curves computed from Equation (17)	79
44 Fracture toughness data for hydrogen-charged 2¼Cr-1Mo base metal, compared with the master curve toughness predictions for uncharged steel	81
45 Fracture toughness data for hydrogen-charged 2¼Cr-1Mo weld metal, compared with the master curve toughness predictions for uncharged material	82
46 Data from Figure 44 after applying a 50 °C temperature shift to account for hydrogen effects	82
47 Data from Figure 45 after applying a 50 °C temperature shift to account for hydrogen effects	83
48 Level 1 pressure-temperature curve for avoiding H-enhanced fast fracture	84
49 Minimum pressurization temperature (MPT) defined as the lower of the subcritical IHAC and the unstable IHAC fracture criteria.	86
50 Critical temperature (T_{IH}) curves for Level 1 and Level 2 MPT assessment	88
51 Through-wall hydrogen concentration profile, illustrating the Level 1 and Level 2 definitions of the maximum-bulk hydrogen concentration for determining T_{IH} from Figure 50	89
52 Determining the maximum crack depth for arrest of IHAC	90
53 Through-wall variation of diffusible hydrogen remote from the crack	91
54 Through-wall variation of total hydrogen remote from the crack.	92
55 Finite element mesh of a 0.2123 in.-deep surface crack in a reactor.	92
56 Finite element mesh of a 0.9315-in.-deep surface crack in a reactor.	93
57 Variation in A_1 during a shutdown/startup transient.	93
58 Level 3 assessment of T_{IH} , given a 0.2123-in.-deep crack	94
59 Level 3 assessment of T_{IH} , given a 0.9315-in.-deep crack	95
60 Comparison of Level 1, 2, and 3 T_{IH} assessments for low-FATT 2¼Cr-1Mo steel	95
61 Comparison of Level 1, 2, and 3 T_{IH} assessments for moderate-FATT 2¼Cr-1Mo steel	96
62 Comparison of Level 1, 2, and 3 T_{IH} assessments for high-FATT 2¼Cr-1Mo steel	96

Tables

1 Summary of K_{IC-H} Results for 2¼Cr-1Mo Base Plate	48
2 Summary of K_{IC-H} Results for 2¼Cr-1Mo Weld Metal	53
3 Material groupings and $\text{FATT}_{\text{Thermal}}$ for Option A	87
4 Material groupings and $\text{FATT}_{\text{Thermal}}$ for Option B	87
5 Material groupings and $\text{FATT}_{\text{thermal}}$ for Option C	87

The Effects of Hydrogen for Establishing a Minimum Pressurization Temperature (MPT) for Heavy Wall Steel Reactor Vessels

1 Executive Summary

Hydrogen, dissolved in the thick wall of a steel pressure vessel during steady-state operation in elevated temperature high-pressure H_2 , can cause both slow-subcritical crack advance, as well as unstable catastrophic fracture during shutdown and startup. This behavior is defined in Section 2. It follows that modern fracture mechanics assessments of the minimum pressurization temperature (MPT) and fitness for service (FFS) must include the deleterious effect of H on both subcritical and unstable internal hydrogen-assisted cracking (IHAC). Two approaches are in draft stage to develop standard procedures that address this need: an API 934-F recommended practice and a WRC Bulletin 562 basis for ASME/API 579.

The objective of this technical report is to establish the technical basis necessary to enable and validate these best practices for quantifying the effects of hydrogen on (a) the MPT, and (b) FFS of a thick wall hydroprocessing reactor. The approach entails two parts. Part 1 emphasizes critical assessment and collection of two primary H-cracking properties: the threshold stress intensity for the onset of subcritical H cracking under slow-rising stress intensity (K_{IH}), and the critical stress intensity for the onset of unstable catastrophic cleavage-like crack growth promoted by H (K_{IC-H}). Part 2 focuses on the methods to use these data to quantitatively to predict an MPT that precludes H cracking during shutdown and startup. The sum of these two parts—validated-extensive IHAC data and science-based engineering analysis—establishes a single technical basis that can be consistently incorporated in API 934-F and API/ASME 579 recommended practices to control H cracking.

Section 3 documents extensive K_{IH} and K_{IC-H} data that conservatively characterize IHAC in $2\frac{1}{4}\text{Cr-1Mo}$ weld metal and base plate. The effects of critical variables are documented; including the degree of temper embrittlement in terms of the FATT after thermal exposure ($FATT_{\text{Thermal}}$), total H concentration, and stressing temperature. K_{IH} data are aggregated for three classes of steel purity: Database A (low purity/high FATT) with $FATT_{\text{Thermal}} > 50^\circ\text{C}$; Database B (intermediate purity/intermediate FATT) with $-30^\circ\text{C} < FATT_{\text{Thermal}} < 50^\circ\text{C}$; and Database C (high purity/low FATT) with $FATT_{\text{Thermal}} < -30^\circ\text{C}$. These three steel composition categories were defined to both recognize the critical interaction of temper embrittlement with hydrogen cracking, and to optimize the combination of existing multiple IHAC data sets from different laboratories. [Alternately, the user can combine databases B and C to quantify IHAC in $2\frac{1}{4}\text{Cr-1Mo}$ steels fabricated before and after (Database A) impurity-chemistry control.]

Subcritical H cracking (Section 3.2) is eliminated below a critical-dissolved H concentration and above a critical temperature, which are related through H-trapping theory to a single-critical parameter. The beneficial effect of increasing temperature is affirmed by fracture mechanics experiments with several specimen geometries, and provides the basis for MPT definition to eliminate subcritical H cracking. Fracture mechanics experiments (Section 3.3) clearly establish that dissolved H can reduce the unstable-fracture toughness of $2\frac{1}{4}\text{Cr-1Mo}$ weld metal and base plate, from K_{IC} to K_{IC-H} , consistent with the deleterious effect of H on Charpy impact energy and Charpy FATT. However, previous studies have not correctly eliminated those data that were improperly interpreted to yield a false K_{IC-H} (e.g. due to the occurrence of innocuous pop-in events).

Validated K_{IC-H} experiments covering a range of H-free FATT values establish that the occurrence of true-unstable crack growth correlates with $(T-FATT_{\text{Thermal}})$, essentially independent of dissolved H concentration and showing a distribution of behavior for a given temperature. H-promoted unstable cracking is eliminated; that is, K_{IC-H} approaches the H-free K_{IC} above a critical temperature equal to (Charpy $FATT_{\text{Thermal}} + 66^\circ\text{C}$) for base plate and above the Charpy impact $FATT_{\text{Thermal}}$ for weld metal. (H-promoted unstable cracking was never observed at absolute temperatures above 86°C for base plate and

above 25 °C for weld metal for the levels of temper embrittlement represented by existing data.) Specific K_{IC} and K_{IC-H} versus temperature data from this analysis are modeled in Section 4 to provide a basis for quantitative MPT determination. Additional data for high-FATT_{Thermal} temper embrittled steels, particularly stressed at temperatures above 50 °C, are required to refine the correlated temperature for the elimination of unstable-H cracking. The factor(s) that control the temperature dependence of K_{IC-H} are not well understood, suggesting the need for improved understanding of the mechanism for H-promoted unstable cracking.

Section 3.4 presents results from a recent API-sponsored study that established the following material-property data relevant to MPT and FFS assessment for V-modified Cr-Mo steel. First, unstable H-cracking is unlikely at ambient temperatures (and above) given the high purity and low FATT_{Thermal}, which are typical of modern Cr-Mo-V, as well as the nil-to-small shift in Charpy FATT due to relatively high dissolved H concentration. Second, V-modified steel does exhibit very slow-stable IHAC for H concentration typical of the high H solubility of this modern steel, but only at relatively high K_{IH} and below a relatively low-critical temperature. Cr-Mo and Cr-Mo-V steels are similarly and significantly susceptible to H cracking when stressed in moderate- to high-pressure H₂ at near ambient temperature (Section 3.5). However, neither steel exhibits a deleterious interaction between IHAC and HEAC. Limited IHAC data have been reported for 1Cr-0.5 Mo, 1.25Cr-0.5Mo, and Cr-0.5Mo steels, but the results are insufficient to support an MPT or FFS assessment.

Section 4 develops the technical basis for MPT and FFS assessments using the fracture mechanics data presented in Section 3. The effects of H concentration, temperature, and cracked body geometry on K_{IH} are effectively modeled based on the fundamental concept of crack tip H concentration similitude: Equal H damage (equal K_{IH}) is created by equal localized crack tip H concentration. For such subcritical crack growth, an H-trapping-based model developed by Al-Rumaih and Gangloff (AG), as well as the engineering model by Anderson and Brown (AB), each use this concept to develop master curves that effectively correlate the large amount of K_{IH} data for each of the three databases of 2½Cr-1Mo steel (Section 4.1). The AG theoretical model fully justifies the AB engineering model, which provides the optimized engineering approach for MPT and FFS assessments aimed to minimize subcritical IHAC.

A scientific model is not available to describe H-promoted unstable cracking. Rather, the FFS procedures for avoiding unstable fast fracture upon shutdown and startup entail a combination of the API 579 Level 2 crack-like flaw assessment, combined with the Wallin Master Curve approach for fracture toughness in the transition region (Section 4.2). In the latter case, the K_{IC-H} versus (T-T₀) Master Curve is conservatively described at the 95 % to 99 % confidence level using a 50 °C (90 °F) temperature increase in the H-free index temperature (T_{0H}), resulting in T_{0H} = FATT_{Thermal}. This temperature shift is based on an examination of the distribution of validated fracture toughness data collected and curated in Section 3.3, and is equally relevant to both base plate and weld metal. These data are insufficient to support a systematic effect of dissolved H concentration on the level of this temperature shift. The H-based shift in Charpy FATT is not used to develop this effect of H on K_{IC-H} versus temperature. For the Level 1 fast fracture assessment, a default pressure-temperature curve was developed to simplify the procedure. If this Master Curve description of K_{IC-H} yields an uneconomical high MPT for a reactor fabricated using an older high FATT_{Thermal} steel, additional experiments may be conducted to measure K_{IC-H} versus temperature for this class of Cr-Mo steel in order to justify a lower MPT.

Section 5 lays out the proposed architecture for the MPT determination, which is defined by both stable IHAC and unstable fast fracture criteria. There are three levels of assessment for each criterion. Level 1 constitutes the simplest and most conservative method, while Level 3 is the most complex procedure and contains the least conservatism. The FFS user may mix assessment levels, depending on the situation. For example, if the MPT is limited by the stable IHAC criterion, the user may combine the Level 1 fast fracture assessment with a Level 2 or 3 stable IHAC assessment.

2 Introduction

Certain types of pressure equipment in refinery service experience increased risk of subcritical crack growth, as well as catastrophic failure during startup and shutdown, due to several service-aging degradation mechanisms. For example, heavy-wall reactor pressure vessels in high-temperature H₂

service can be susceptible to hydrogen-assisted cracking near ambient temperature. Atomic hydrogen that dissolves in the reactor wall during elevated temperature operation remains in the steel during a shutdown cycle. Dissolved hydrogen at or near ambient temperature can result in two undesirable outcomes: 1) subcritical hydrogen-assisted crack growth and 2) unstable fast fracture due to a reduction in fracture toughness caused by hydrogen. (Dissolved H can also reduce steel tearing resistance in the resistance curve sense; however, assessment of this form of stable cracking is beyond the scope of this technical report.) The refining industry reduces the likelihood of these outcomes through adherence to a minimum pressurization temperature (MPT). The intent of the MPT is to ensure that the vessel is not subject to above-threshold primary stresses from pressure at temperatures where the material of construction is susceptible to hydrogen cracking.

Developing standard procedures for determining safe MPTs is a high priority for the API Committee on Refinery Equipment (CRE). Two parallel efforts within API have resulted in somewhat conflicting methodologies for specifying MPTs for pressure equipment. The Subcommittee on Corrosion and Materials drafted Recommended Practice 934-F, which covers heavy-wall reactors in high-temperature hydrogen service. The Joint API/ASME Committee on Fitness-for-Service (FFS), which developed and maintains the API 579-1/ASME FFS-1 standard (also known as API 579), has drafted comprehensive rules for determining the MPT in *all* pressure equipment that operates at elevated temperatures. Welding Research Council (WRC) Bulletin 562 contains the procedures that have been proposed for inclusion in API 579. The WRC 562 methodology differs significantly from the procedures set forth in the draft API 934-F document and supporting-final reports to the 934-F Task Group. The former is based on quantitative fracture mechanics principles pertinent to broad-based FFS assessments, with a particularly strong treatment of H-free fracture toughness, while the latter contains a science-based procedure for specifying the MPT governed by hydrogen.

The CRE has requested that the present authors prepare a technical report to provide guidance on the effects of hydrogen on fast fracture and slow stable crack growth, as they pertain to steel pressure vessels having a degradation of mechanical properties by temper and hydrogen embrittlement. The overarching objective of this report is to establish the technical basis necessary to validate the best practices for quantifying the effect of hydrogen on (a) the minimum pressurization temperature, and (b) fitness-for-service of a specific thick wall hydroprocessing reactor. These recommendations will be in a form that can be consistently adapted by the committees responsible for API 934-F and API 579.

3 Critical Review of Experimental Data for Hydrogen Effects On 2 ¼ Cr-1 Mo Steel

3.1 Background

3.1.1 Terminology

Extensive laboratory research initiated in the late 1970s establishes that atomic H, predissolved during elevated temperature exposure in high pressure H₂, enables hydrogen cracking (often referred to as hydrogen embrittlement) of Cr-Mo alloy steels during shutdown and startup. This deleterious effect of H is captured by fracture mechanics-based experiments, with typical material properties schematically characterized in Figure 1.

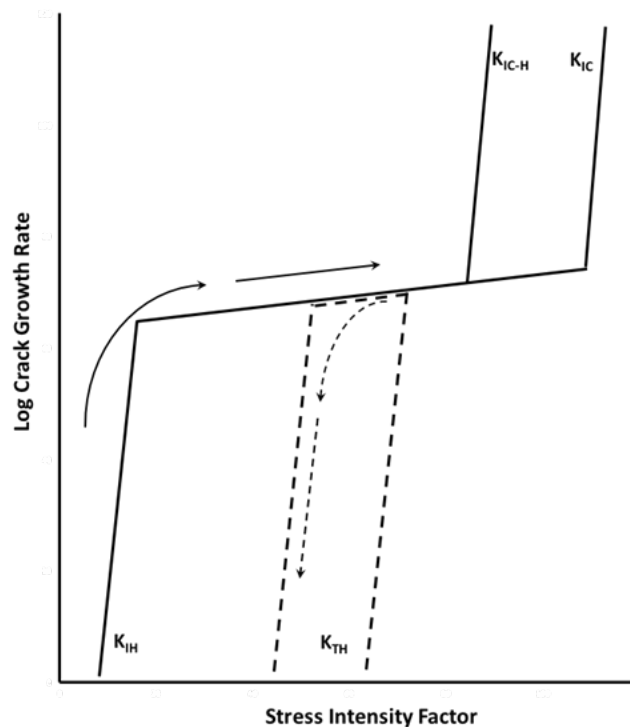


Figure 1—Schematic diagram of the effect of loading format on the IHAC and HEAC of low-alloy Cr-Mo steels, noting the material properties relevant to fracture mechanics assessment of minimum pressurization temperature and fitness-for-service

This is the so-called internal hydrogen assisted cracking (IHAC) problem, and it is often assessed for H-precharged steel stressed in moist air. IHAC involves a unique microscopic fracture path that is either intergranular or transgranular, and not microvoid-based. The low values of K_{IH} in Figure 1, and these brittle-crack paths, were at the time surprising for Cr-Mo steels in petrochemical applications, owing to the moderate strength of such alloys and limited or compromised fracture mechanics data.

From Figure 1, the following material property terms are relevant to MPT and FFS modeling of this deleterious effect of H.

- K_{IH} : the threshold stress intensity factor for the onset of subcritical crack growth under slow-rising crack mouth opening displacement (CMOD) and rising stress intensity (K);
- da/dt versus K : the rate of subcritical crack propagation (da/dt) under either rising CMOD (with rising K) or under fixed CMOD (with falling K);
- K_{TH} : the threshold stress intensity factor for the arrest of a slowly propagating crack under fixed CMOD and declining K . Crack arrest may be immediate or after an increment of stable crack extension at fixed CMOD. The value of K_{TH} may depend on the K level at which the CMOD is fixed.
- K_{IC-H} : the critical stress intensity for the onset of unstable-rapid crack propagation, under either rising or fixed CMOD, in the presence of dissolved H.
- K_{IC} : the plane strain fracture toughness in the absence of H, and typical of either cleavage or microvoid-based cracking depending on temperature.

For IHAC, these properties may depend on H concentration, degree of temper embrittlement, loading rate (dK/dt), temperature, and steel product form/microstructure. Additionally, the presence of gaseous hydrogen can degrade the steel by hydrogen environment assisted cracking (HEAC), including possible

interaction with IHAC. In this situation, the partial pressure of H_2 , presence of other molecules (e.g. O_2 , H_2S , C_2H_4 , and C_2H_2) in the environment, and temperature are critical variables. Systematic laboratory measurements of these material properties for IHAC and HEAC, as a function of the cited variables, are required input for quantitative MPT and FFS assessments of Cr-Mo steels in thick-wall pressure vessels and H_2 service. These measurements are complex, and a critical literature review is necessary to establish validated and relevant databases.

3.1.2 Chronology of Experimental Research

The chronological progression of fracture mechanics laboratory experiments and modeling work, which is critically reviewed in ensuing sections to establish specific input data for MPT/FFS modeling, is captured by the following timeline for H embrittlement of H-precharged Cr-Mo steel, predominantly the $2\frac{1}{4}Cr-1Mo$ grade.

- Research in the early 1980s by the Japanese and French identified the strong possibility that K_{IH} under slow-rising CMOD is substantially less than K_{TH} that is classically reported for constant CMOD loading leading to crack arrest.^[1-3] These data are shown in Figure 2, where the compact tension (CT) specimen was H precharged in elevated temperature high pressure H_2 .^[2] This subcritical-H cracking was either intergranular or transgranular (likely through bainite interfaces). The data in Figure 2 provide the basis to assume that yield strength and tempering temperature are, at most, secondary factors that are not likely to impact K_{IH} for IHAC in $2\frac{1}{4}Cr-1Mo$. The fundamental mechanism for the damaging effect of slow-rising crack tip strain on subcritical H crack growth was not established, and questions persisted as to whether this behavior was an experimental artifact.^[1-3]
- Early research lead by Sakai demonstrated the unexpected result that precharged H degraded the Charpy V-notch (CVN) energy measured under impact loading in the ductile-to-brittle transition regime. Data suggested that the Charpy fracture appearance transition temperature (FATT) increased by $10^\circ C$ per weight part-per-million (wppm) of predissolved H.^[4, 5] The mechanism for the unexpected deleterious effect of H on unstable fast fracture was not established and questions existed as to whether this behavior was an experimental artifact.
- These initial studies (a) identified the controlling deleterious interaction of temper embrittlement with H embrittlement, each driven by service exposure,^[3, 5] (b) defined the expected H concentration dependence of K_{IH} ,^[3] and (c) suggested that H embrittlement may be reduced above a critical temperature.^[3, 6]

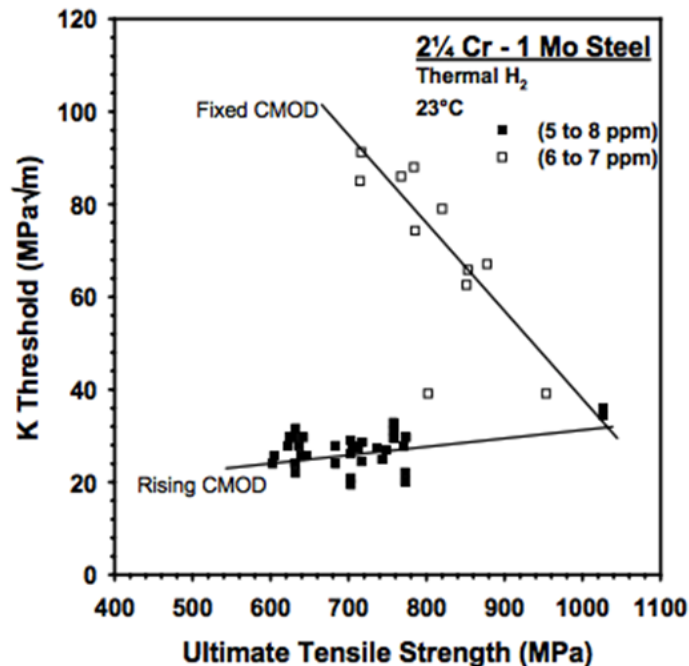


Figure 2—The ultimate tensile strength dependence of the threshold stress intensity for the onset of IHAC under slow-rising CMOD loading (K_{IH}) compared to the arrest of IHAC under fixed-CMOD (K_{TH} under decreasing K) loading for H-precharged 2 $\frac{1}{4}$ Cr-1Mo steel stressed at 25 °C

- Into the early 1990s, Japanese and French researchers provided fracture mechanics analyses of the impact of predissolved H on MPT and FFS, as governed by both subcritical IHAC as well as H-promoted unstable crack propagation. [7–10]
- As fracture mechanics test methods matured, a laboratory procedure was proposed to accurately and precisely measure pressure vessel relevant K_{IH} and da/dt versus elastic-plastic stress intensity factor (K). [11]
- A joint industry program (JIP; Phase I led by A. Bagdasarian) was conducted in the 1990s wherein Japan Steel Works, Kobe Steel Company, and Creusot Loire Steel Company laboratories used the proposed fracture mechanics method [11] in over 80 experiments to measure K_{IH} , da/dt versus K , K_{TH} , and occurrence of H-enhanced unstable fracture at K_{IC-H} . [12] Testing used gold-coated 25 mm thick compact tension specimens to minimize H loss during prolonged testing, particularly at elevated temperature. Measured-dissolved H concentration and the elastic-plastic fracture mechanics test method were validated by extensive interlaboratory testing for a single low-J heat of 2 $\frac{1}{4}$ Cr-1Mo base plate, and the effects of H concentration, rising-CMOD rate, and test temperature were characterized. The interaction of temper embrittlement and H embrittlement was characterized using 10 lots of 2 $\frac{1}{4}$ Cr-1Mo base plate and weld metal, temper embrittled by either long-term service exposure or by standardized-laboratory step cooling. A wide range of Cr-Mo purity and degree of temper embrittlement ($FATT_{Thermal}$) was investigated.
- The resulting database from this Phase I JIP is a critical resource for MPT/FFS modeling, as captured in a final report that was never published in the open literature. [12] These data provided the foundation for Anderson's development of REACT software to model H effects on pressure vessel FFS. [13]
- In the late 1990s, Japanese researchers developed an important test method for K_{IH} , da/dt versus K , and K_{IC-H} measurement using a very thick (88.9 mm) H-precharged compact tension specimen. [14, 15] This work minimized H loss during testing, and thus provided an additional capability to measure the

effect of temperature on these H cracking properties. Hydrogen cracking measurements using this test method provided the basis for a patented FFS methodology.^[16]

- A Phase II JIP lead by D.L. Cooke was conducted in the early 2000s to focus on two issues of extreme importance to assessing the effects of H on MPT/FFS: (a) the beneficial role of test temperature on subcritical H cracking and (b) the extent of H-enhanced unstable fracture in the ductile-to-brittle transition regime. A single moderate-impurity weld metal produced by Kobe Steel was examined ($X_B = 25$ wppm to 29 wppm and FATT after step-cooled temper embrittlement = 28 °C to 45 °C), and the resulting database is a critical input for MPT/FFS modeling.
- For Part A of this Phase II JIP, a novel slotted compact tension specimen was developed in order to continuously supply H from the slot surface to the crack tip, replicating H supply to a reactor-wall flaw and without H loss at higher temperatures.^[17] The beneficial effect of increasing temperature in reducing subcritical H cracking was definitively demonstrated. This work led to a proposed crack tip damage-mechanism model, which predicted threshold H concentration and temperature conditions where subcritical H cracking was eliminated.^[18] This work associated the mechanism for elimination of IHAC with reduced H concentration trapped along the crack path and above a critical temperature.
- For Part B of this Phase II JIP, the temperature dependencies of both subcritical and unstable H-cracking in the weld metal produced by Kobe was examined by (a) Kobe Steel Company using a standard 25-mm-thick compact tension specimen^[19–21] and (b) Japan Steel Works using the 90-mm-thick compact tension specimen.^[22,23] Both studies presented validated quantitative fracture mechanics data showing that H can promote unstable crack propagation in Cr-Mo steel. Each study demonstrated that increasing temperature reduced both subcritical and unstable forms of H-cracking, given by both increasing K_{IH} and K_{IC-H} with increasing temperature.
- An API-sponsored study was initiated in 2009 to develop a recommended practice (RP 934-F) to quantify H effects on MPT for thick-wall reactor operation. This work developed two separate approaches to modeling the temperature and H concentration dependencies of K_{IH} . Gangloff extended the crack tip fracture process zone damage model, previously developed with Al-Rumaih,^[24] while Anderson and Brown proposed an empirical approach based on the analogy between the use of elastic K to define the governing crack tip stress distribution, and that of a crack tip H concentration parameter.^[25] Each approach was based on the similitude concept of equal K_{IH} produced for equal-local H concentration, sensitive to steel-temper embrittlement and temperature but independent of cracked body geometry. These models are summarized and compared in Section 4.1; each approach is strengthened by the results of the other to provide a single, useful MPT/FFS tool.
- The API-sponsored study was extended in 2012 to investigate H cracking in 2¼Cr-1Mo-¼V base plate and weld metal, and demonstrated the substantial improvement in H cracking resistance exhibited by this modern (high purity) steel.^[26–29]
- In parallel with these recent API-sponsored studies, Pillot and co-workers extended the early French work, led by Coudreuse, and particularly focused on the effect of H in promoting unstable fracture in the ductile-to-brittle transition regime with the aim of predicting MPT for thick-wall reactor operation.^[30–34] This work extends the pioneering efforts of Sakai and co-workers.^[4]
- In parallel with these recent API-sponsored studies, several Japanese researchers employed modern elastic-plastic fracture mechanics methods, coupled with direct current electrical potential measurement of crack growth, to develop quantitative K_{IH} and da/dt data for 2¼Cr-1Mo, with and without V addition.^[35–40] This work employs the approach first used in the Phase I JIP program.^[12]
- Collectively, these studies establish that conservative MPT and FFS assessment of Cr-Mo steel in thick-wall reactor applications should focus on two material properties, K_{IH} and K_{IH-C} , as a function of temperature for steels of varying temper embrittlement. Rising-CMOD loading is emphasized as the most severe-conservative condition following Figure 1. The aim of the proposed MPT and FFS assessments detailed in Section 4 and applied in Section 5 is to establish the temperatures above which either of the following does not occur: (a) slow-subcritical crack propagation governed by K_{IH}

and (b) fast-unstable H cracking governed by K_{IC-H} for a given steel composition. Crack growth rate is not considered in this MPT/FFS assessment. However, such data are available in several of the cited references (i.e. 3, 12, 16, and 24) should the user desire to quantify crack growth extension per shutdown and startup temperatures below the critical level where subcritical IHAC is otherwise eliminated.

Key papers in the progression of studies summarized in this section have been critically reviewed to establish a broad database of K_{IH} and K_{IC-H} versus degree of temper embrittlement, predissolved H concentration, and temperature.

3.1.3 Steel Compositions

The literature represented in the timeline of Section 3.1.2 establishes that the fracture mechanics properties that characterize H cracking of steels for thick wall petrochemical reactor applications are overwhelmingly focused on (a) the 2¼Cr-1Mo composition and (b) heat-treated base plate and weld metal product forms. We are not aware of any fracture mechanics laboratory studies of IHAC or HEAC associated with (a) a specific microstructural area of a single- or multi-pass weld heat affected zone (HAZ) or (b) a dissimilar metal weld (DSMW) interface, i.e. between 2¼Cr-1Mo and an austenitic stainless steel. Given this lack of experimental data on H cracking, plus the variety of defects that could be associated with a DSMW interface, it is not possible to provide a recommendation on the proper K_{IH} and K_{IC-H} data to use for MPT or FFS assessment. If a reactor failure analysis associates an H crack with a specific welded interface or HAZ microstructure, H cracking experiments must be commissioned to determine the extent to which K_{IH} and K_{IC-H} vary from the values given in Databases A, B, and C. The technology exists to conduct these experiments.^[12,27]

Quality data are emerging to characterize IHAC in modern 2¼Cr-1Mo-¼V, as reported in Section 3.4. Older steels that may be encountered in legacy heavy wall reactor structures include C-0.5Mo, 1Cr-0.5Mo, and 1¼Cr-0.5Mo-Si. The microstructures of these steels are ferritic (with various morphologies, including bainite or martensite), and contain carbides (cementite and M_xC_y , where M may be Mo or Cr) depending on alloy content and thermomechanical processing.

It is reasonable to assume that these lower-alloyed Cr-Mo steels are susceptible to IHAC, but data are limited. Predissolved H degrades tensile ductility and Charpy impact energy for 1Cr-0.5Mo^[4] and C-0.5Mo.^[41] Moreover, it is well known that low-strength C-Mn steels, with ferrite-carbide microstructures, are susceptible to IHAC and HEAC.^[42,43,44,45] Tempered martensitic steels, such as AISI 4130 (up to 1.1Cr and 0.25Mo), are also well known to be susceptible to IHAC and HEAC.^[46] Early work by Task Group II of the Japanese Pressure Vessel Research Council confirmed this expectation and reported K_{IH} results for a variety of petrochemical steels with H-free fracture toughnesses (K_{IC}) above 150 MPa√m at 25 °C.^[1] Each steel (C-0.5Mo, ½Cr-0.5Mo, 1Cr-0.5Mo, 1¼Cr-0.5Mo-Si, and 3Cr-Mo) was significantly susceptible to IHAC. K_{IH} at 25 °C equaled 53 MPa√m for the ½Cr, 1Cr and 1¼Cr steels, in both the stress relieved and laboratory step cooled conditions. K_{IH} equaled 47 MPa√m for 2¼Cr-1Mo and 35 MPa√m 3Cr-1Mo, each in the step-cooled condition; for these two steels, K_{IH} decreased somewhat to these levels due to temper embrittlement. Neither the precharged and post-test H concentrations (initially in the likely range of 1.3 wppm to 3 wppm) nor the exact H charging method (elevated temperature H₂ or H₂S saturated acetic acid solution at 25 °C), nor the applied dK/dt and effect of plasticity on K, nor FATT were specified for each steel. K_{IH} was defined by the first divergence of the load-displacement curve from H-free reference behavior. While IHAC is clearly demonstrated, these uncertain experimental conditions and relatively high K_{IH} for 2¼Cr-1Mo compared to the data in Figure 2 compromise the usefulness of these data for quantitative MPT and FFS assessment. The original Japanese reports may detail these experimental conditions; however, it is unlikely that lower-alloy steels were examined over the range of $C_{H-Total}$ and temperature that is needed to support the MPT and FFS analyses presented in Sections 4 and 5.

The API 934-F draft states:^[47]

This RP also can be used to develop an MPT curve for reactors fabricated from 1¼Cr-½Mo and 1Cr-½Mo steels. In general, a reactor fabricated from 1¼Cr-½Mo or 1Cr-½Mo steel would be expected to operate at lower temperatures and lower hydrogen partial pressures than either a reactor fabricated from 2¼Cr-1Mo steel or V-modified 2¼Cr-1Mo steel. As a result, it would

typically be less affected by temper embrittlement and hydrogen embrittlement, resulting in less-restrictive limits based on an MPT curve developed from guidance provided in this document (which is specific to 2¼Cr-1Mo)."

The first part of this statement on lower operating temperature and hydrogen pressure is correct, and it is known that the 1¼Cr grade exhibits lower $FATT_{Thermal}$ values compared to 2¼Cr-1Mo.^[48] However, the latter claim of a less-restrictive MPT curve is speculative and must be viewed with caution. The MPT assessment outlined in Section 5 for 2¼Cr-1Mo is based on values of the thermally exposed FATT ($FATT_{Thermal}$) and includes the total H concentration ($C_{H-Total}$) dissolved in the steel at reactor-operating temperature and H₂ pressure. If an accurate value of this $FATT_{Thermal}$ is known^[48] (or estimated from steel composition^[49]) for a given purity of 1¼Cr-½Mo or 1Cr-½Mo,^[48] and if $C_{H-Total}$ is known for a reactor temperature and H₂ pressure, a Section 5 assessment of MPT using the 2¼Cr-1Mo K_{TH} or K_{IC-H} database is not necessarily "less restrictive." That is, increased resistance to temper embrittlement and reduced H uptake are explicitly accounted for through use of $FATT_{Thermal}$ and $C_{H-Total}$ in the 2¼Cr-1Mo database. At issue is the extent to which these IHAC and H uptake/transport properties for these lower-alloy steels (K_{IH} , K_{IC-H} , and $C_{H-Total}$ versus temperature and H₂ pressure) differ compared to 2¼Cr-1Mo properties for fixed $FATT_{Thermal}$ and $C_{H-Total}$. The limited K_{IH} values given in the previous paragraph for the lower-alloy steels show that temper embrittled 2¼Cr-1Mo may exhibit somewhat lower K_{IH} , but the comparison is compromised by uncertain experimental conditions and accuracy. Moreover, it is necessary to scale these laboratory H cracking data to an MPT, using a fracture mechanics similitude model of the sort presented in Sections 4 and 5. The shape of the K_{IH} and K_{IC-H} dependencies on temperature are important in these analyses, and may vary for the lower-alloy steels compared to 2¼Cr-1Mo. (For example, Iwamoto determined that MPT for H-free 2¼Cr-1Mo equaled the $FATT_{Thermal}$ but, in contrast, equaled $FATT_{Thermal} + 20\text{ °C}$ for 1¼Cr-½Mo, 1Cr and ½Mo steels owing to the temperature dependence of K_{IC} [8]). For these reasons, it is not possible to make a stronger quantitative recommendation with regard to MPT and FFS assessments for 1¼Cr-½Mo and 1Cr-½Mo, since the necessary steel-properties data are not available to conduct a Section 4–5 analysis. The experimental capabilities exist to obtain such data, if necessary, to support MPT and FFS analyses.^[12,27]

The focus of the ensuing discussion centers on 2¼Cr-1Mo and 2¼Cr-1Mo- V base plate and weld metal. If data for lower alloy Cr-Mo steels are identified or measured, then the MPT and FFS methods proposed in Section 5 for 2¼Cr-1Mo may be revised and applied as needed.

3.1.4 Hydrogen Solubility and Diffusivity in 2¼ Cr-1 Mo(V)

The literature was reviewed to define the best H solubility and H diffusivity properties for 2¼Cr-1Mo(V) steels, as needed for MPT and FFS assessment (Sections 4 and 5). Variability in each property is possible, given the strong role of H trapping and its complicating impact on the analysis of H concentration measurements, which are challenging to obtain.

3.1.4.1 Hydrogen Solubility

The H₂ pressure and temperature dependence of H concentration is given by:

$$C_{H-Total} = S_{Eff} (T) f_{H_2}^{1/2}$$

where S_{Eff} is the effective H solubility, which depends on temperature (T), and f_{H_2} is H fugacity, which is a known function of H₂ pressure (P_{H_2}). Three experimentally based solubility relationships were reported for 2¼Cr-1Mo base plate:

$$C_{H-Total} = 0.592 \exp(-27,080 \text{ (kJ/mol)} / RT) P_{H_2}^{1/2} \quad (\text{Koers et al.})^{[50]}$$

$$C_{H-Total} = 0.469 \exp(-26,570 \text{ (kJ/mol)} / RT) P_{H_2}^{1/2} \quad (\text{Pillot et al.})^{[51]}$$

$$C_{H-Total} = 0.811 \exp(-27,080 \text{ (kJ/mol)} / RT) P_{H_2}^{1/2} \quad (\text{Sakai et al.})^{[4]}$$

where R is the gas constant, and the measured heat of the solution is given for each study. For each equation, H concentration is in mol H/m^3 Fe (1 mol H/m^3 = 0.128 wppm H) and H_2 pressure is in Pa. For exposure at 425 °C (698 °K) and 2000 psi H_2 (13.78 MPa and assuming that P_{H_2} equals f_{H_2}), these equations give the following values of $C_{H-Total}$: 2.7 wppm (Koers et al.^[50]), 2.3 wppm (Pillot et al.^[51]), and 3.7 wppm (Sakai et al.^[4]). For the Phase I JIP-relevant (see the next paragraph) exposure at 468 °C (741 °K) and 2700 psi H_2 (18.6 MPa and assuming that P_{H_2} equals f_{H_2}), these equations give the following values of $C_{H-Total}$: 4.0 wppm (Koers et al.^[50]), 3.5 wppm (Pillot et al.^[51]), and 5.5 wppm (Sakai et al.^[4]). Hydrogen solubility data are not broadly available for weld metal.

It is recommended that the Sakai et al. relationship be used to estimate the total concentration of H dissolved in 2¼Cr-1Mo steel, since it is conservative relative to the older Koers et al. equation and the more modern relationship from Pillot et al. The values measured by Pillot and co-workers are reasonably considered to be the most accurate by virtue of their careful H_2 charging and autoclave removal procedures, as well as modern H concentration measurement method. However, the Sakai et al. relationship is justified as more accurate based on extensive-replicate H concentration measurements made during the Phase I JIP.^[12] Specifically, for the latter set of H_2 pressure and temperature conditions listed in the previous paragraph, the average of the $C_{H-Total}$ values measured from 26 specimens of a low J (40) 2¼Cr-1Mo base plate was 5.0 wppm, with a range of values between 3.7 wppm and 5.7 wppm.^[12] (These specimens were gold coated for H retention during IHAC testing, but it is assumed that this surface condition did not affect H solubility in the steel.) These experimental results show that the Sakai et al. equation provides an accurate-conservative prediction of H solubility (5.5 wppm), compared to the predictions of Koers et al. (4.0 wppm) and Pillot et al. (3.5 wppm), as well as the predicted average of all three relationships (4.3 wppm). This comparison justifies the recommendation that the Sakai et al. equation be used for MPT and FFS assessments. Notably, the present draft of API 934-F^[47] uses this Sakai et al. relationship for S_{Eff} ,^[4] which is acceptable, while WRC 562^[49] proposes to use the Koers et al. relationship for S_{Eff} ,^[50] which should be revised to the Sakai et al. equation.

The solubility of H in 2¼Cr-1Mo base plate is increased due to V addition. The most definitive values were given by Pillot and co-workers for 2¼Cr-1Mo-¼V:^[32,51]

$$C_{H-Total} = 0.036 \exp[-6,943 (kJ/mol) / (RT)] P_{H_2}^{1/2}$$

where H concentration is in mol H/m^3 Fe and H_2 pressure is in Pa. For exposure at 425 °C and 2000 psi H_2 , this equation gives a $C_{H-Total}$ of 5.2 wppm. The higher H solubility of 2¼Cr-1Mo-¼V compared with 2¼Cr-1Mo (3.7 wppm from Sakai et al.) was experimentally verified.^[26,27] The H solubility in V -modified Cr-Mo at high exposure temperatures typical of reactor operation should be somewhat dependent on steel-aging temperature. Data are not available for weld metal. Both the API 934-F and the WRC 562 drafts use this solubility relationship for V -modified steel.

3.1.4.2 Hydrogen Diffusivity

Three important studies provide D_{Eff} versus temperature data for 2¼Cr-1Mo base plate that are essentially identical. Specifically:

$$D_{Eff} (cm^2/s) = 2.4 \times 10^{-3} \exp(-17,725 (kJ/mol) / RT) \quad (\text{Sakai et al.})^{[4]}$$

$$D_{Eff} (cm^2/s) = 2.3 \times 10^{-3} \exp(-16,940 (kJ/mol) / RT) \quad (\text{Koers et al.})^{[50]}$$

$$D_{Eff} (cm^2/s) = 3.4 \times 10^{-3} \exp(-19,390 (kJ/mol) / RT) \quad (\text{Pillot et al.})^{[51]}$$

The D_{Eff} values are 1.9×10^{-6} cm²/s (25 °C) and 7.9×10^{-6} cm²/s (100 °C) from the Sakai et al. equation^[4], 2.5×10^{-6} cm²/s (25°C) and 9.8×10^{-6} cm²/s (100 °C) from the Koers et al. equation^[50], and 1.4×10^{-6} cm²/s (25 °C) and 6.6×10^{-6} cm²/s (100 °C) from the Pillot et al. equation^[51]. Data have not been reported for weld metal. Any one of these H diffusivity relationships may be used in FFS assessment. The present draft recommendations in API 934-F^[47] and WRC 562^[49] similarly use the Koers et al. relationship for D_{Eff} .^[50]

Hydrogen diffusivity in V-modified 2¼Cr-1Mo base plate is less well known; existing data show that D_{Eff} is strongly reduced near ambient temperatures due to H trapping at nano-scale VC. Reasonable values were reported by Pillot and co-workers for 2¼Cr-1Mo-¼V:

$$D_{\text{Eff}} \text{ (cm}^2 \text{ / s)} = 8.0 \times 10^{-4} \exp(-24,975 \text{ kJ / mol / RT}) \quad (\text{Pillot et al.})^{[51]}$$

$$D_{\text{Eff}} \text{ (cm}^2 \text{ / s)} = 6.7 \times 10^{-3} \exp(-30,035 \text{ kJ / mol / RT}) \quad (\text{Pillot et al.})^{[32]}$$

The D_{Eff} are $3.4 \times 10^{-8} \text{ cm}^2/\text{s}$ (25 °C) and $2.6 \times 10^{-7} \text{ cm}^2/\text{s}$ (100 °C), compared to $3.7 \times 10^{-8} \text{ cm}^2/\text{s}$ (25 °C) and $4.2 \times 10^{-7} \text{ cm}^2/\text{s}$ (100 °C) for these first and second equations, respectively. It is likely that effective H diffusivity depends on steel aging temperature, if altering VC size, number density, and interface coherence. The present draft recommendations in API 934-F^[47] and WRC 562^[49] each use the first relationship for D_{Eff} .^[51]

3.1.5 Classes of 2¼Cr-1Mo Composition and Temper Embrittlement

The resistance of 2¼Cr-1Mo (and most low-alloy steels) to IHAC and HEAC falls as the degree of intergranular temper embrittlement rises, as quantified by a rising-compositional parameter, ψ ($\psi = \text{Mn} + 0.5\text{Si} + \text{S} + \text{P}$ in atomic pct).^[52] Paralleling this trend, for thick wall reactor steels, rising temper embrittlement is correlated with increasing (a) impurity composition (given by $J = 10,000(\text{Si}+\text{Mn})(\text{P}+\text{Sn})$ in wt pct or $X_B = 0.01(10\text{P} + 5\text{Sb} + 4\text{Sn} + \text{As})$ in weight ppm (wppm) and (b) elevated temperature service exposure often simulated in the laboratory by an accelerated-standardized step cooling procedure.^[33] The J factor has been widely used for 2¼Cr-1Mo base plate, while X_B characterizes weld metal as well as alloy steels (such as the 1¼Cr grade) that contain intentionally high Si.

Steel purity has increased over time, as shown in Figure 3, which gives the distribution of J versus year the steel was purchased for a specific reactor fabrication.^[8] The historical data in Figure 3 (top) provided a J-factor basis for Iwamoto to suggest generations 1 through 4 of 2¼Cr-1Mo, where mean J falls from 230 to 150, 100, and 60 in wt pct, with improving melt practice.¹ The results in Figure 3 suggest that (a) the upper limits on J and X_B are 310 wt pct and 25 wppm (and perhaps as high as 30 wppm) for 52 base plate heats and 11 weld metal heats, respectively, for the oldest reactors in service (as captured by these particular base plate and weld metal compilations), and (b) IHAC resistance increases for increasingly modern Cr-Mo steels due to reduced temper embrittlement (decreasing J and X_B). However, each Cr-Mo steel generation exhibits a broad distribution of J values, necessitating a statistical analysis that estimates J for a specific-reactor MPT or FFS assessment.

The dependence of temper embrittlement on J and X_B has been typically characterized by the Charpy $\text{FATT}_{\text{Thermal}}$ of a given steel after either in-service exposure or laboratory step cooling (Figure 3.4).² The distribution of measured $\text{FATT}_{\text{Thermal}}$ values is broad for a given J, but statistical analysis of the mean and 95 % or 99 % upper bound estimates of service exposed $\text{FATT}_{\text{Thermal}}$ versus J are used for estimates of

¹ An alternate definition of the generations of steel purity in this paper was based on an MPT equaling the temperature for the onset of upper shelf ductile fracture.^[3,8] The resulting categories are: (1st) with $J > 300$ wt pct and MPT above 177 °C, (2nd) $J = 300$ wt pct and MPT = 149 °C, (3rd) $J = 180$ wt pct and MPT = 121 °C, and (4th) $J < 100$ wt pct and MPT = 66 °C. These MPT estimates do not include the effect of H.

² Less-extensive data were presented to show the $\text{FATT}_{\text{Thermal}}$ dependence on X_B for 1¼Cr-½ Mo steel, and J was correlated with X_B for 2¼Cr-1Mo weld metal.^[3,8]

an MPT to avoid brittle fracture without dissolved H.^[33,48] These equations may be used to associate a mean or 95 % upper bound of the service-exposed $FATT_{Thermal}$ for the mean J of each steel generation.³

A valid concern was cited by J.E. McLaughlin during technical report review. That is, the results in Figure 4 include a group of high-J values that are above the upper limit for the specific operating reactor steels represented in Figure 3. The origin of these high-J factors was not discussed in the original reporting of Figure 4.^[33] However, McLaughlin speculates that such high J may be associated with either laboratory heats used in research studies or to the errant use of J to characterize reactor-weld metal purity that contains Si not included in X_B correlation. If it is concluded that legacy-reactor steels never exhibit J above 310 wt pct (and X_B above 25 wppm to 30 wppm), the $FATT_{Thermal}$ versus J data in Figure 4 can be reanalyzed to define new statistical correlations for MPT and FFS assessments when specific-measured $FATT_{Thermal}$ data are not available. This point does not impact the IHAC data presented in this technical report because actual J and X_B results, as well as measured $FATT_{Thermal}$, are consistently reported. However, McLaughlin's view does impact the way in which individual IHAC data are aggregated to form databases for MPT and FFS assessments. This point is considered in an ensuing section on the collection of IHAC data for the various impurity/ $FATT_{Thermal}$ classes of 2¼Cr-1Mo.

³ Hydrogen cracking data in this technical report are correlated with the Charpy-based $FATT_{Thermal}$ for Cr-Mo steels; however, some users may only have ductile-to-brittle transition temperature (DBTT) data for a given steel. The $FATT$ is typically above the DBTT, with the difference increasing from just above 0 °C to about 10 °C with increasing degree of temper embrittlement. This trend, plus deviation at very high J, is illustrated by the following comparison using JPVRC data for 2¼Cr-1Mo base plate provided to the 934-F Task Group by Akitada and Tahara. (1) For J = 95 wt pct, $FATT$ is -75 °C and -54 °C before and after step cooling, while DBTT is -74 °C and -59 °C before and after step cooling. (2) For J = 186 wt pct, $FATT$ is -35 °C and -14 °C before and after step cooling, while DBTT is -38 °C and -23 °C before and after step cooling. (3) For J = 344 wt pct, $FATT$ is -4 °C and 46 °C before and after step cooling, while DBTT is -8 °C and 53 °C before and after step cooling.

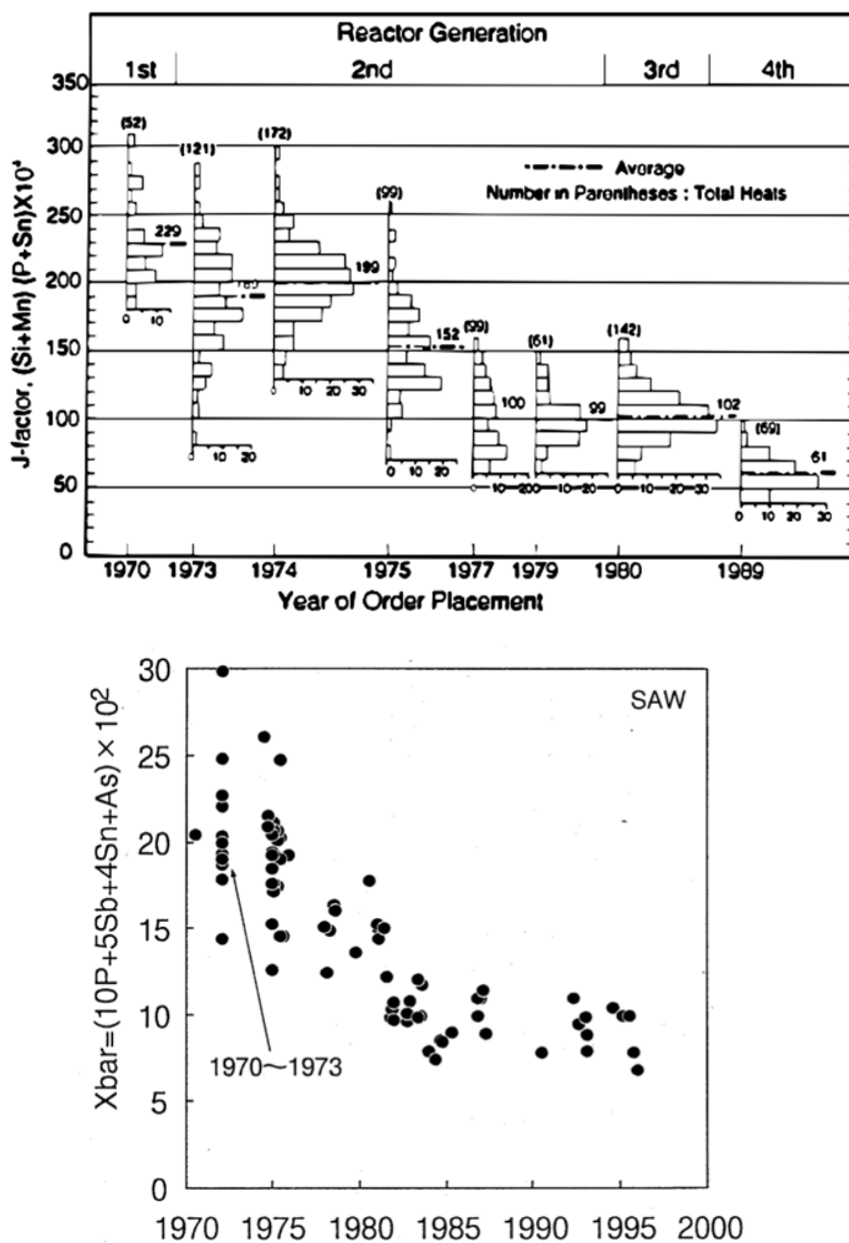


Figure 3—Historical record of improving $2\frac{1}{4}Cr-1Mo$ purity provided by: (top) Japan Steel Works for base plate; *After Iwadate*^[8] and (bottom) Kobe Steel Company for weld metal.^[12] In this plot, J is in weight pct and X_B is in wppm. The X_B on the ordinate, with the coefficient of 10^2 , is calculated using impurity concentrations in weight pct rather than wppm.

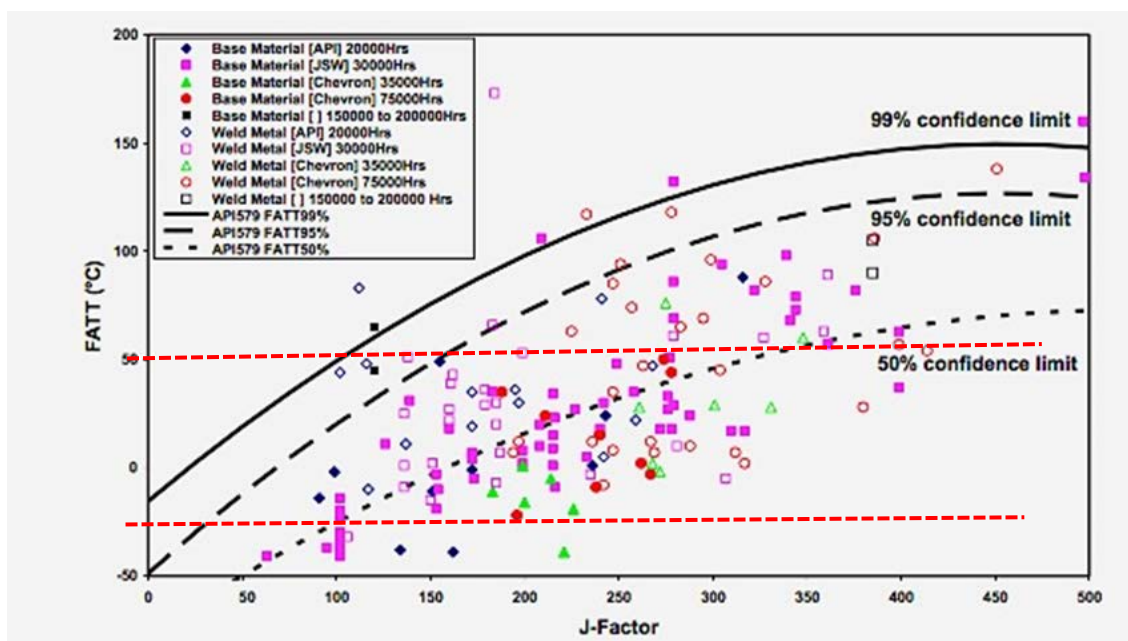


Figure 4—Relationship between $FATT_{Thermal}$ and J for Cr-Mo steels subjected to long-term in-service exposure showing the occurrence of temper embrittlement.^[33] The dotted lines illustrate the three classes of IHAC database developed in this study.

For IHAC characterization, the members of the Phase I JIP categorized 2¼Cr-1Mo base plate and weld metal into three groups according to the following ranges, which were taken to encompass either service exposed commercial heats or step cooled laboratory heats of steels actually used in the experimental testing program:^[12]

High J/ X_B	$250 < J < 480$	$23 < X_B < 40$	$25^{\circ}\text{C} < \text{thermally exposed } FATT < 90^{\circ}\text{C}$
Mid J/ X_B	$100 < J < 250$	$10 < X_B < 23$	$-25^{\circ}\text{C} < \text{thermally exposed } FATT < 25^{\circ}\text{C}$
Low J/ X_B	$J < 100$	$X_B < 10$	$\text{thermally exposed } FATT < -25^{\circ}\text{C}$

These categories are somewhat arbitrary owing to the large variability in measured J and $FATT_{Thermal}$ for given lots of steel, consistent with Figure 4. ⁴ For this reason, the IHAC data collected in this technical report are always associated with specific-reported J or X_B and $FATT_{Thermal}$.

In addition to the variability in FATT data, there are two challenges to a reactor MPT or FFS analysis. First, measured steel/reactor service-specific values of $FATT_{Thermal}$ are often not available, even based on laboratory step cooling correlation using the as-fabricated steel. Therefore, it is necessary to estimate $FATT_{Thermal}$ using measured J through the distributions in Figure 4, and perhaps even based on estimated J or X_B through the dependence on steel vintage (Figure 3). Such estimation of X_B for weld metal is particularly problematic owing to a lack of data. Second, the IHAC database developed in ensuing sections is not sufficient to define a smooth-functional dependence of K_{IH} and K_{IC-H} on $FATT_{Thermal}$ (or on J or X_B). Rather, it is necessary to combine the results of multiple laboratory studies of IHAC into bins.

⁴ For example, a service exposed plate (125,000 h) was characterized by J of 140 wt pct, but a measured $FATT_{Thermal}$ of 130°C . A service exposed (230,000 h) weld metal exhibited a measured $FATT_{Thermal}$ of 149°C and X_B of 15 wppm.^[3,12]

The present technical report establishes that validated-literature data can be reasonably aggregated to develop an IHAC database for each of three purity/FATT categories of 2½Cr-1Mo steel base plate and weld metal. IHAC data are collected and combined for steels that exhibit these specific ranges of FATT_{Thermal} (measured after thermal exposure, explicitly reported, and not inferred from steel J or X_B):

High FATT base plate and weld metal	39 °C < FATT _{Thermal} < 200 °C	Database A
Mid FATT base plate and weld metal	6 °C < FATT _{Thermal} < 37 °C	Database B
Low FATT base plate and weld metal	-90 °C < FATT _{Thermal} < -28 °C	Database C

These FATT_{Thermal} ranges can be simplified for MPT or FFS analysis to control IHAC. Specifically, a steel of known FATT_{Thermal} is reasonably (above the Database A to B boundary) and conservatively (below the Database B to C boundary) associated with one of these three-strong IHAC databases.

Database A (high impurity/FATT)	FATT _{Thermal} > 50 °C
Database B (intermediate purity/FATT)	-30 °C < FATT _{Thermal} < 50 °C
Database C (high purity/low FATT)	FATT _{Thermal} < -30 °C

These FATT_{Thermal} bounds are shown by the horizontal-dotted lines in Figure 4. Since the relationship between FATT_{Thermal} and J is an empirical distribution, these database bounds can be restated in terms of J for the 95th percentile case using the trend lines in Figure 4: ⁵

Database A (high impurity/FATT)	J > 155 wt pct
Database B (intermediate purity/FATT)	30 < J < 155 wt pct
Database C (high purity/low FATT)	J < 30 wt pct

or for the 50th percentile case:

Database A (high impurity/FATT)	J > 340 wt pct
Database B (intermediate purity/FATT)	95 < J < 340 wt pct
Database C (high purity/low FATT)	J < 95 wt pct

⁵ This connection between the IHAC-data driven categories, bounded in terms of measured FATT_{Thermal}, compared to the categories bounded in terms of known/estimated J, may be compromised by issues in Figure 4. Specifically, this correlation appears to include high impurity laboratory heats of 2½Cr-1Mo not relevant to legacy reactors, which exhibit a maximum J of 310 wt pct (Figure 3) and the use of J rather than X_B to characterize high Si weld metal. The user of the MPT and FFS approaches recommended in Sections 4 and 5 should consider the importance of these points in a specific reactor problem.

These three databases will yield three levels of MPT that systematically step decrease with increasing purity from Database A to Database C. The detailed K_{IH} data to justify this statement are given in Section 3.2, and the MPT analysis is specified in Section 4. These three Cr-Mo steel categories are defined based on a reasonable aggregation of existing-valid IHAC data, and not on classes of reactor steels that are in service. That is, this database separation is justified by published IHAC data, which was the charge of this technical report analysis. The use of three databases will result in step-function changes in the calculated MPT, as necessitated by the existing IHAC data. The user will have to judge the proper IHAC database that is relevant to the steel under consideration, and perhaps employ “what if?” calculations for a steel near a database boundary. Alternately, the user could predict an MPT for each database, smooth the step function of MPT versus $FATT_{Thermal}$, and interpolate an MPT for the specific steel and $FATT_{Thermal}$ under study.

McLaughlin concludes that Database A is populated by IHAC results obtained for highly impure laboratory-model steels, with J values above the highest level typical of operating reactors (maximum J of 310 wt pct, Figure 3) that exhibit a mean $FATT$ above 50 °C. Rather than databases A, B, and C, McLaughlin suggests that only databases B and C are necessary for MPT and FFS analysis. In his view, Database B effectively represents those 2¼Cr-1Mo steel base plates and weld metals, which were fabricated without chemistry control. Database C effectively represents steels fabricated under the chemistry control specified in API 934-A and/or company procedures. This two-database approach hinges on the assumption that Figure 3 captures the purities of all generations of hydroprocessing reactors. Fortunately, these two approaches to IHAC database development are in no way contradictory. The user can determine if Database A is useful for their steel of interest, provides a conservative upper bound on MPT, or is a basis for “what if?” calculations. If the steel of interest falls within databases B or C, both categorizations based on either IHAC data or reactor-steel fabrication chemistry control/history will yield exactly the same MPT result.

Summarizing this discussion, K_{IH} results are correlated in Section 3.2 for multiple steels within each of three databases defined by IHAC-study reported $FATT_{Thermal}$. K_{IC-H} is considered in Section 3.3 as a function of specific $FATT_{Thermal}$ for any steel. Service exposed $FATT_{Thermal}$ is emphasized because of its proxy relationship to impurity content and thermal exposure, which fundamentally govern temper embrittlement and thus IHAC,^[51] as well as because of its correlative relevance to K_{IC-H} . For a specific reactor problem, if $FATT_{Thermal}$ is known based on direct measurement, or is statistically estimated^[33,48] using known J/X_B , this value is used to select the appropriate IHAC database to identify K_{IH} and K_{IC-H} master curves. If only the year of steel fabrication is known, the data in Figure 3 can be used to estimate a mean or 95th percentile J or X_B .^[48] that is then statistically related to the relevant $FATT_{Thermal}$ (e.g. Figure 4). In this approach, it is not necessary to define a reactor generation, which lumps a wide distribution of $FATT_{Thermal}$ into a single class. Other approaches (for example, adherence to API 934-A chemistry control) to relating the year of reactor fabrication to anticipated $FATT_{Thermal}$ (or $DBTT_{Thermal}$) are appropriate if supported by data and experience.

3.2 Subcritical Hydrogen Cracking Threshold Stress Intensity (K_{IH})

3.2.1 Experimental Considerations

Laboratory characterization of the damaging effect of H represented in Figures 1 and 2 has evolved so that a fracture mechanics-capable test laboratory can accurately measure the properties relevant to MPT and FFS assessment. The procedure implemented in the Phase I JIP,^[12] and refined in a recent API-sponsored experimental program,^[27] provides the detailed prescription for such measurements.

The following experimental issues were considered in selecting the valid K_{IH} data that are presented and analyzed in ensuing sections. Data were ignored if they did not adequately address these points.

- The Charpy $FATT_{Thermal}$ should be reported for the laboratory step cooled or service exposed condition of the steel studied, so as to capture the deleterious effect of temper embrittlement on IHAC. ($FATT$ is emphasized in IHAC database development since this property, as well as J and X_B , were consistently reported in the H-cracking studies. $DBTT$ was not typically reported. This fact may necessitate a correlation between $DBTT$ and $FATT$, if only the former is known, when the IHAC databases are used in MPT or FFS assessment [Section 4].)

- The applied CMOD rate (dK/dt) must be sufficiently slow to guarantee a conservative loading rate-independent value of K_{IH} .
- Care should be taken to avoid H loss during specimen removal from the elevated temperature H_2 autoclave, as well as during ambient temperature storage and handling prior to testing.^[27] The starting and final H concentrations should be measured, with a companion charging block and a core from the cracked specimen, respectively, particularly for long-time and/or elevated temperature experiments where H loss from Cr-Mo can be substantial. Hot extraction (at about 600 °C) is preferred compared to melt extraction. In the present data analysis, judgment is exercised with regard to defining the most accurate and K_{IH} -relevant H concentration. Either the initial $C_{H-Total}$ or the average of the initial and final values of $C_{H-Total}$ is used for the database and modeling reported in this technical report.
- The onset of subcritical crack growth should be accurately measured, ideally with direct current electrical potential (dcPD). Moreover, care should be taken to minimize the impact of false crack growth indication due to the effect of rising-CMOD crack tip plasticity on steel resistivity.
- Ideally, both elastic K and elastic-plastic K values should be reported, with the latter calculated following a modern-accurate J integral assessment of the plastic part of K. However, caution was exercised with the elastic-plastic K analysis, as inaccuracies are possible. Experience with the often-used 25-cm-thick compact tension specimen demonstrates this uncertainty, but suggests that the elastic-only K is sufficiently accurate for values up to 60 MPa $\sqrt{m}$.^[12] Higher levels of K applied to this CT specimen are suspect, unless a validated analysis is employed to determine the plastic component of the J-integral.
- Ideally, da/dt should be measured versus K, sufficient to predict the extent of slow stable IHAC for shutdown/startup at temperatures below T_{CRIT} and K above K_{IH} . However, the focus of the present MPT and FFS assessment does not include subcritical crack growth.
- The important effect of elevated temperature on IHAC is particularly important. Recent results using a novel-slotted compact tension specimen, gold-coated 25-mm-thick CT specimens, and very large (90-mm-thick) CT specimens are emphasized because these approaches minimize H loss during rising-CMOD testing.

3.2.1.1 Hydrogen Charging Environment

The majority of K_{IH} data for 2½Cr-1Mo have been obtained using compact tension specimens that are H precharged by elevated temperature exposure in high-pressure H_2 , paralleling reactor conditions. Potentially useful K_{IH} and K_{IC-H} data were reported for H precharging in H_2S -bearing acid solutions at 25 °C. We consider that these results are relevant to MPT/FFS assessment and are included in the databases presented in this section. In his review of this technical report, McLaughlin cautions that such data may be invalid because the H_2S electrolyte introduces permanent-fissure damage that could reduce K_{IH} and K_{IC-H} characteristic of dissolved H only. Such fissure-damage is presumably not relevant to IHAC during startup or shutdown of a hydroprocessing reactor. While this concern is important to assess, we do not believe that the issue has sufficient merit to disqualify the K_{IH} and K_{IC-H} data obtained using wet H_2S -precharged CT specimens. The following analysis supports this position.

McLaughlin did not provide evidence for the occurrence of HIC-type fissure damage in 2½Cr-1Mo exposed to wet H_2S at 25 °C. While H_2 pressurization of an interface in steel can create a fissure, a preexisting-fissure nuclei must exist, typically in the form of a large-cracked inclusion or interface.^[53] This feature is provided by stringered-MnS/MnSiO₄ inclusions in C steel, which provide an ideal-large site for H_2 accumulation in the well-known HIC and SOHIC problems.^[53] This feature is not common in modern 2½Cr-1Mo base plate or weld metal CT specimens, but cannot be ruled out for older Cr-Mo steels. The important requirement for a large, preexisting defect to nucleate H_2 -pressurization damage is demonstrated by calculations that quantify fissure- H_2 pressurization during slow cooling of H precharged 2½Cr-1Mo.^[50] Fissure growth is only predicted if the preexisting fissure is 2 mm diameter or larger. This feature is unlikely to be present in a 2½Cr-1Mo steel laboratory specimen, unless the steel contains a substantial distribution of large inclusions.^[53] Fissuring due to H_2 pressurization at large-inclusion

interfaces was reported by Shewmon for a Si-killed C-Mn steel and by McCray for an early C-½Mo steel, each exposed in high temperature-high pressure H₂ service below the hydrogen attack threshold.^[54,55] As such, even if fissures form during 25 °C wet H₂S-H precharging of older 2¼Cr-1Mo steels, any lowering of K_{IH} or K_{IC-H} for IHAC could actually parallel fissuring-IHAC interaction during in reactor service.

Theoretical consideration of H solubility sheds light on the use of acidic H₂S-bearing solutions for H precharging, as a proxy to elevated temperature H₂ exposure. Experiments show that immersion in H₂S saturated acetic acid at 25 °C produces a total-measured H concentration of 1 wppm to 3 wppm in 2¼Cr-1Mo, which is about a factor of 2 less than H uptake into C-Mn steel^[1,10,17,56,57] Moreover, it is not correct to conclude that 1 wppm to 3 wppm H in Cr-Mo steel is sufficient to produce H₂ fissure damage. Rather, it is necessary to define the portion of this C_{H-Total} that is soluble in the steel lattice and independent of H trapping for “open system”^[58] charging in wet H₂S. It is this lattice H concentration that establishes the equilibrium H₂ pressure in a fissure through Sievert's Law. A calculation was performed to estimate interface H₂ pressure in pure Fe in equilibrium with NACE TM0177 solution at 25 °C (assuming pH 3 and free corrosion potential of -700 mV_{SCE}). Lattice H concentration in pure Fe in this solution (H⁺/H overpotential = -272 mV) is estimated to equal 0.05 wppm.^[59] Using Sievert's Law for H in Fe,^[58] the H₂ pressure in equilibrium with this lattice H concentration is 2250 MPa at 25 °C. For a 0.05 mm to 0.1 mm diameter preexisting penny-shaped crack/defect, this level of internal pressure produces a K of 13 MPa√m to 18 MPa√m. This calculation suggests that wet H₂S exposure may produce fissures by interface IHAC in Cr-Mo, but only if a relatively large incipient defect is present for pressurization, and only if dK/dt for pressurization loading is finite so as to favor a K_{IH} near 20 MPa√m (Figure 2). This H₂ pressure is somewhat uncertain since the overpotential for H production in NACE solution likely varies by 30 mV to 50 mV, and lattice-H concentration depends on overpotential.^[59] As a final complication, experiments show that H charged from wet H₂S solution at 25 °C produces dislocations, defects (atomic vacancies and vacancy clusters), and, in the limit, perhaps microcracks from coalesced vacancies.^[60,61] The H trapped at such defects is much higher than the lattice-H solubility and is a major component to measured C_{H-Total}. (This trapped H is not available for defect pressurization.) The details of these atomic-to-micro-scale defects are likely different for H charging at 25 °C compared to 450 °C. Such defects could affect K_{IH} and K_{IC-H}, following McLaughlin's concern but by a very different mechanism.

Experiments are required to determine the effect of an H precharging environment on K_{IH} and K_{IC-H} given these uncertainties regarding (a) the size/distribution of incipient defects in various vintages of 2¼Cr-1Mo steel, (b) the magnitude of defect pressure levels, and (c) the effect of environment on H-defect production. The following experimental results do not support the concern regarding wet H₂S precharging of H.

- Pillot reports that modern-pure 2¼Cr-1Mo does not exhibit resolvable-macroscopic fissure damage in a hydrogen induced cracking (HIC) test.^[62] Refined experiments are in progress to probe for micro-scale H₂ pressurization damage from wet H₂S.
- A comprehensive JPVRC summary paper did not report fissure-type damage in various hydroprocessing reactor alloy steels H precharged in wet H₂S.^[1] This charging condition produced a C_{H-Total} of 1.3 wppm, comparable to elevated temperature pressurized H₂. Both charging environments were employed to characterize IHAC.^[1] There was no report of an effect of the H-precharging environment on K_{IH}, even though a focus was on comparing these electrochemical and gaseous charging methods. There was no report that K_{IH} from electrolytic charging is irrelevant to reactor MPT and FFS analyses.
- Pillot and co-workers examined the effect of the H charging method on IHAC in a low-FATT_{Thermal} lot of 2¼Cr-1Mo. ^[63] For a 2¼Cr-1Mo base plate (FATT_{Thermal} = -100 °C), exposure in H₂S saturated acidic chloride solution (NACE TM0177) produced C_{H-Total} of 1.9 wppm to 2.1 wppm in CVN specimens, comparable to H uptake during elevated temperature exposure in H₂. H outgassing at 20 °C was identical, independent of the H charging method, which suggests that neither fissure H₂ nor lattice-scale defect trapped H forms were present. Both NACE TM0177 solution and elevated temperature H₂ precharging produced (a) the same increase in CVN FATT_{Thermal} for constant C_{H-Total} of 2 wppm, (b) the same K_{IH} for constant C_{H-Total} of 2.5 wppm to 3.0 wppm, and (c) the same H-reduced K versus crack extension R-curve for constant C_{H-Total} of 2.5 wppm to 3.0 wppm. H-promoted unstable cracking was not observed for either H-precharging solution.

Pillot's study focused on a modern-pure steel; however, there is no evidence to support the speculation that H₂S-driven fissuring (or H-defect generation) uniquely occurs in high impurity 2¼Cr-1Mo that may contain large MnS and MnSiO₄ inclusions.^[54]

- Sakai and co-workers reported the same increase in FATT_{Thermal} for wet H₂S and elevated temperature H₂ charging of what is likely to be older-impure 2¼Cr-1Mo, but steel composition was not specified.^[4]
- Data collected in ensuing sections show that essentially identical K_{IH} values are produced at a given C_{H-Total}, established by either elevated temperature H₂ or ambient temperature wet H₂S precharging. This result is true for each of the three 2¼-1Mo impurity/FATT_{Thermal} classes examined.

These theoretical considerations and experimental results justify use of either an H₂S bearing electrolyte or elevated temperature H₂ for H-precharging fracture mechanics specimens used in K_{IH} and K_{IC-H} determination. This is a conservative approach because, if wet H₂S promotes either H₂ pressure fissures or atomic defects, measured values of K_{IH} and K_{IC-H} should be less than those measured for elevated temperature H₂ charging. Nonetheless, such K_{IH} and K_{IC-H} values are clearly marked in the data collection of this technical report. With this background, a critical emphasis of this technical report is to collect IHAC data that are reported by several laboratories for reasonably common test conditions (slow dK/dt, measured C_{H-Total}, FATT_{Thermal} category, temperature, and dK/dt).

3.2.2 Base Case Data for 2¼Cr-1Mo Steel

Example IHAC data are presented to provide a basis for characterizing the effects of H concentration and temperature on K_{IH} (and da/dt) for 2¼Cr-1Mo base plate and weld metal.

The reality that slow-rising CMOD uniquely produces severe IHAC in low-J (modern) 2¼Cr-1Mo base plate and weld metal, at 25 °C, is demonstrated by the Phase I JIP data in Figure 5.^[12] These results from a single compact tension specimen conform to the schematic behavior in Figure 1 and the early data in Figure 2. First, K_{IH} is much less than K_{TH} and is a small fraction of the H-free K_{IC}. Above K_{IH}, da/dt rises with increasing K during rising CMOD. Upon entering the CMOD hold, da/dt falls rapidly to 0 with modest-to-nil subcritical crack growth. For this particular experiment with high purity base plate, there is no evidence of H-promoted unstable cracking; therefore, K_{IC-H} must exceed 70 MPa√m (the point where the rising CMOD was fixed).

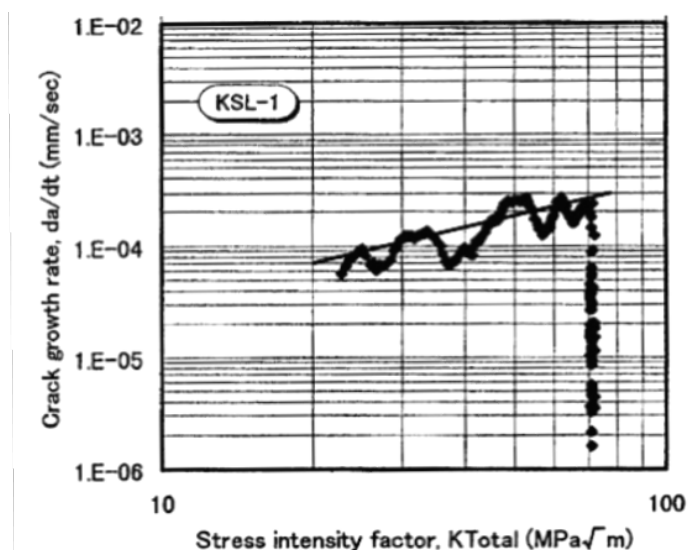


Figure 5—Effect of loading format on IHAC for low-J base plate of 2.48%Cr-1.10%Mo (J = 40, FATT_{Thermal} after step cool = -90°C, σ_{YS} = 447 MPa), precharged with a total-H concentration of 5.7 wppm, then stressed in moist air under slow-rising CMOD (dK/dt = 0.007 MPa√m/s) at 25 °C. The rising CMOD was fixed after rising to the highest K plotted and crack growth arrested with steeply falling da/dt during a 100 h exposure. The total H concentration measured at the end of the experiment was 2.7 wppm. The trend line is da/dt = 3.8 × 10⁻⁶ K^{1.02} for the units in this plot.^[12]

Figure 6 demonstrates the wide range of applied dK/dt where K_{IH} is low and constant for high-purity base plate and weld metal (of both low and moderate purities). These data show a reasonable lower bound on K_{IH} (22 MPa $\sqrt{m}$ to 28 MPa $\sqrt{m}$), which persists to dK/dt as high as 0.4 MPa $\sqrt{m/s}$ for this high-total H concentration of 5 wppm and high-purity base plate. The high-purity weld metal and impure weld metal each conform to a single dependence of K_{IH} on dK/dt . However, it is possible that the upper dK/dt , where K_{IH} rises above a plateau, decreases with decreasing steel purity. The data are not sufficient to establish this loading rate interaction with steel temper embrittlement. Nonetheless, the results in Figure 6 provide a conservative lower bound if specific dK/dt -dependent K_{IH} is required for a high-level FFS analysis. The databases developed in an ensuing section were typically defined for a single dK/dt of 0.007 MPa $\sqrt{m/s}$, which is relevant to slow shutdown and startup conditions for a thick-wall reactor.

Figure 7 shows that da/dt during rising CMOD is directly proportional to the applied dK/dt for the base plate and weld metals in Figure 6. The present analysis is limited to MPT and FFS assessments based on K_{IH} . Use of the crack growth rate to assess subcritical crack extension per shutdown/startup is not examined.

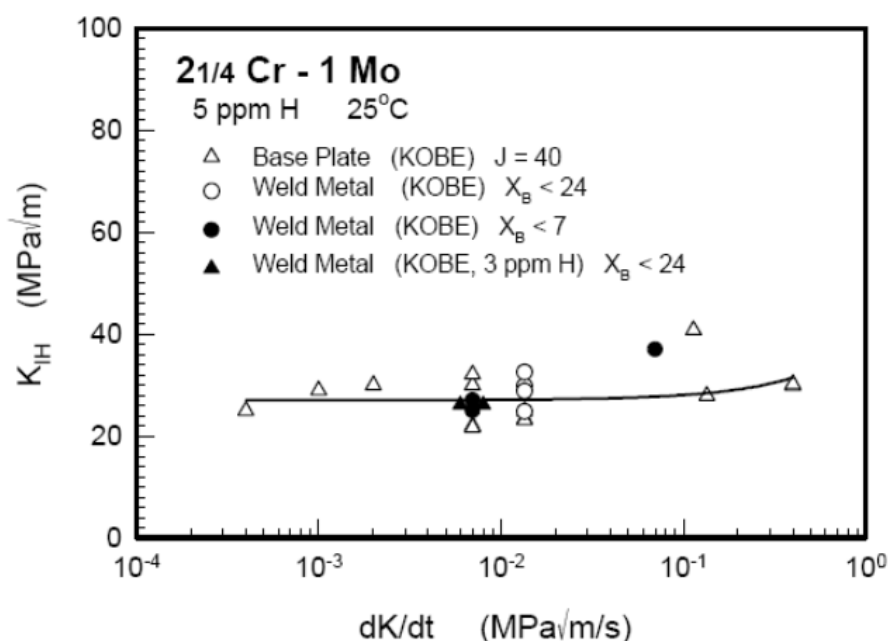


Figure 6—Effect of loading rate on K_{IH} for the low-J base plate in Figure 5, plus data for low X_B weld metal (step cooled FATT_{Thermal} = -57°C) and moderate X_B weld metal (step cooled FATT_{Thermal} = 32°C) with the indicated-predissolved total H concentration.^[12] The trend line is $K_{IH} = 27.0 \exp(0.38 dK/dt)$ for the units in this plot.

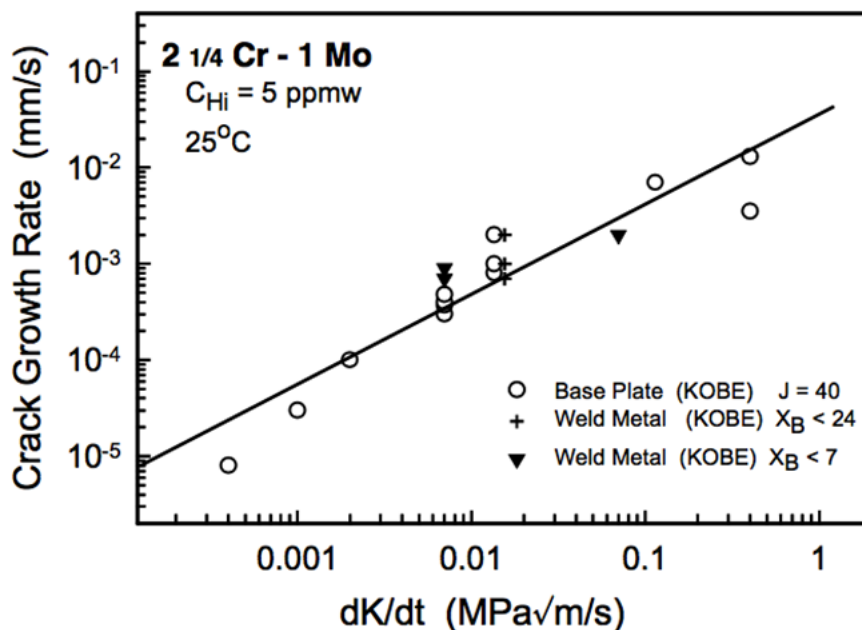


Figure 7—Effect of loading rate on the da/dt during rising CMOD, at K midway between K_{IH} and the highest K in the loading, for the base plate, two weld metals, and H concentrations shown in Figure 6.^[12] The trend line is $\log da/dt = -1.52 + 0.96 \log (dK/dt)$ for the units in this plot.

3.2.3 Effects of H Concentration and Temperature for Similitude Modeling

Detailed quantitative characterization of the effects of H concentration, temperature, and degree of temper embrittlement on the rising-CMOD threshold stress intensity for the onset of IHAC, K_{IH} , are central to conservative MPT and FFS modeling of a thick-wall reactor. Substantial high-quality literature data exist to meet this need for 2½Cr-1Mo base plate and weld metal, as established in the following sections and applied in Sections 4 and 5.

3.2.3.1 Effect of H Concentration at 25 °C

In measuring and modeling the effect of dissolved H concentration, it is important to recognize that the total H concentration ($C_{H-Total}$) is the sum of deeply (near-irreversibly) trapped H and diffusible H (C_{H-Diff}) concentrations. The C_{H-Diff} is the sum of the H concentration present in normal interstitial lattice sites (C_L) and mobile-trapped H that is in equilibrium with one or more low to moderate binding energy (E_B) states in the Cr-Mo steel microstructure.^[52] The details of these various H solubilities in Cr-Mo steels were discussed by Al-Rumaih.^[17] The K_{IH} values presented in the ensuing sections are correlated with $C_{H-Total}$. (Modeling presented in Sections 4 and 5 focuses on C_{H-Diff} , because this H concentration fundamentally controls H cracking.) The effect of H concentration on K_{IH} is established by aggregating data for each of the three impurity classes of 2½Cr-1Mo base plate and weld metal.

3.2.3.1.1 Low FATT 2½Cr-1Mo

All validated K_{IH} versus $C_{H-Total}$ data for low FATT 2½Cr-1Mo base plate and weld metal are presented in Figure 8 for slow-rising CMOD loading of precharged compact tension specimens in moist air at 23 °C. Specific data were extracted from: (a) the Phase I JIP study^[12], including Kobe Common Base Plate with step cooled $FATT_{Thermal} = -90$ °C ($J = 40$ wt pct), JSW In House #3 Base Plate with step cooled $FATT_{Thermal} = -45$ °C to -61 °C ($J = 37$ wt pct), Shell Scotsford Base Plate with service exposed $FATT_{Thermal} = -28$ °C ($J = 54$ or 133 wt pct), Kobe High Purity Weld Metal with step cooled $FATT_{Thermal} = -57$ °C ($X_B < 7$ wppm), and JSW In House #4 Base Plate with step cooled $FATT_{Thermal} = -42$ °C ($J = 154$ wt pct)^[12], (b) experiments conducted for BP with a single lot of base plate with step cooled $FATT_{Thermal} = -84$ °C ($J = 50$ wt pct)^[25], (c) an interlaboratory program carried out for the Japanese Pressure Vessel

Research Council with steel of unknown composition, but neither step cooled nor service exposed so as to be effectively equivalent to a low FATT steel [3,12], and (d) by Japan Steel Works using 90-mm-thick CT specimens of a step cooled base plate with FATT = -76°C (95 wt pct) loaded at a particularly slow dK/dt of $0.0005\text{ MPa}\sqrt{\text{m/s}}$.^[15] All other experiments in (a) through (c) were conducted with 25-mm-thick CT specimens at a dK/dt of $0.007\text{ MPa}\sqrt{\text{m/s}}$. All experiments in (a), (b), and (d) employed elevated temperature H_2 precharging of H; the JPVRC work in (c) may have used wet H_2S precharging, but the reporting does not establish this detail.

In this correlation, the initial $C_{\text{H-Total}}$ was used as typically reported based on companion test cube measurements, and assuming minimal H loss during handling and loading prior to K_{IH} measurement. This approach is justified by the fact that, for the Phase I JIP data, measured-final $C_{\text{H-Total}}$ for these relatively short-term tests was essentially equal to starting-target values.^[12] When these rising-CMOD experiments were ended with a long-term (100 h to 120 h) hold time after K_{IH} , the final-measured $C_{\text{H-Total}}$ is much less than the H concentration present at K_{IH} . Moreover, the JPVRC and BP studies (Figure 3) only reported target-initial $C_{\text{H-Total}}$. The trend line for $C_{\text{H-Total}}$ above 1.5 wppm is based on linear regression, while the steeply sloped line is qualitatively drawn. For $C_{\text{H-Total}}$ above 5 wppm, K_{IH} may be interpreted as an H-concentration independent lower bound with a mean value of $28\text{ MPa}\sqrt{\text{m}}$. Notably, a single correlation is observed between K_{IH} and $C_{\text{H-Total}}$, as measured in this wide variety of experiments. These results are part of Database C, which is applied in an ensuing section.

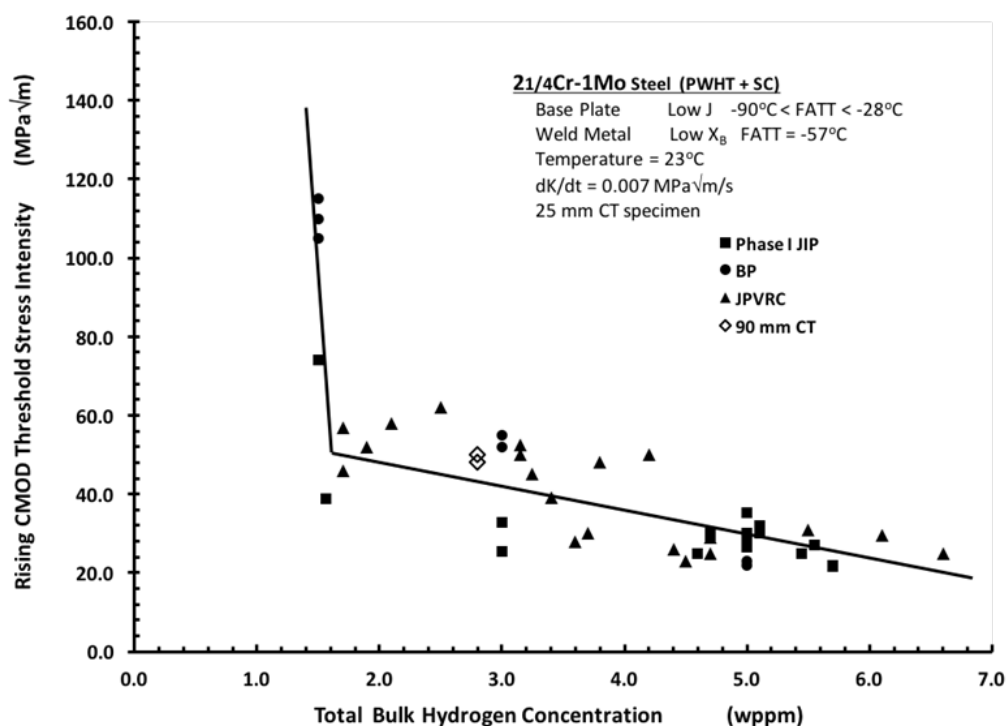


Figure 8—Effect of total-dissolved H concentration, produced by elevated temperature exposure in high-pressure H_2 , on the elastic K_{IH} for high-purity (low J and X_B) weld metal and base plate of $2\frac{1}{4}\text{Cr-1Mo}$ stressed in moist air at a single-slow-rising CMOD and 23°C . Specific J and X_B values for each base plate and weld metal are listed in the text. These results contribute to Database C.⁶

⁶ Iwadata, Nomura, and Watanabe established the dependence of K_{IH} on $\text{FATT}_{\text{Thermal}}$ for $2\frac{1}{4}\text{Cr-1Mo}$ base plate that was H precharged in H_2S bearing acetic acid solution providing a $C_{\text{H-Total}}$ of 2 wppm to 2.6 wppm. CT specimens were subjected to slow-rising CMOD at 25°C .^[3,7] These H_2S -based results are consistent with the H-based data in Figure 8: (a) at $\text{FATT}_{\text{Thermal}}$ of -40°C , $K_{\text{IH}} = 70\text{ MPa}\sqrt{\text{m}}$, and (b) at $\text{FATT}_{\text{Thermal}}$ of 0°C , $K_{\text{IH}} = 55\text{ MPa}\sqrt{\text{m}}$. A specimen precharged in H_2 ($C_{\text{H-Total}}$ of 4.2 wppm) yielded $K_{\text{IH}} = 40\text{ MPa}\sqrt{\text{m}}$ at $\text{FATT}_{\text{Thermal}}$ of -60°C . These K_{IH} values were defined at the first deviation from the H-free steel load-CMOD curve, and are therefore somewhat higher than the more precise data presented in Figure 8.^[3,11,3,12]

3.2.3.1.2 Moderate FATT $2\frac{1}{4}\text{Cr-1Mo}$

All validated K_{IH} versus $C_{H\text{-Total}}$ data for moderate FATT $2\frac{1}{4}\text{Cr-1Mo}$ base plate and weld metal are presented in Figure 9 for slow-rising CMOD loading of precharged 25-mm-thick compact tension specimens in moist air at 25 °C. These specific data were obtained during the Phase I JIP using 25-mm-thick CT specimens that were H precharged in elevated temperature H_2 .^[12] In this correlation, the initial $C_{H\text{-Total}}$ was used as reported based on test cube measurements, and assuming minimal H loss during handling and loading prior to K_{IH} measurement. This approach is justified by the fact that, for the Phase I data, measured-final $C_{H\text{-Total}}$ levels for short-term tests were essentially equal to starting-target values, while those for long-term tests were low due to the prolonged (typically 100 h) hold time after K_{IH} was defined. These results contribute to Database B.

The data in Figure 9 are limited for stressing at 25 °C. The horizontal trend line is drawn through the mean ($K_{IH} = 28 \text{ MPa}\sqrt{\text{m}}$) of the existing data at and above 3 wppm H, assuming no dependence on $C_{H\text{-Total}}$, while the upward sloping trend for lower H concentrations is an estimate. Additional data, obtained with different fracture mechanics specimens and at other temperatures, better resolve this behavior as cited in an ensuing section. Additional data were obtained with different fracture mechanics specimens and at other temperatures, as cited in an ensuing section.

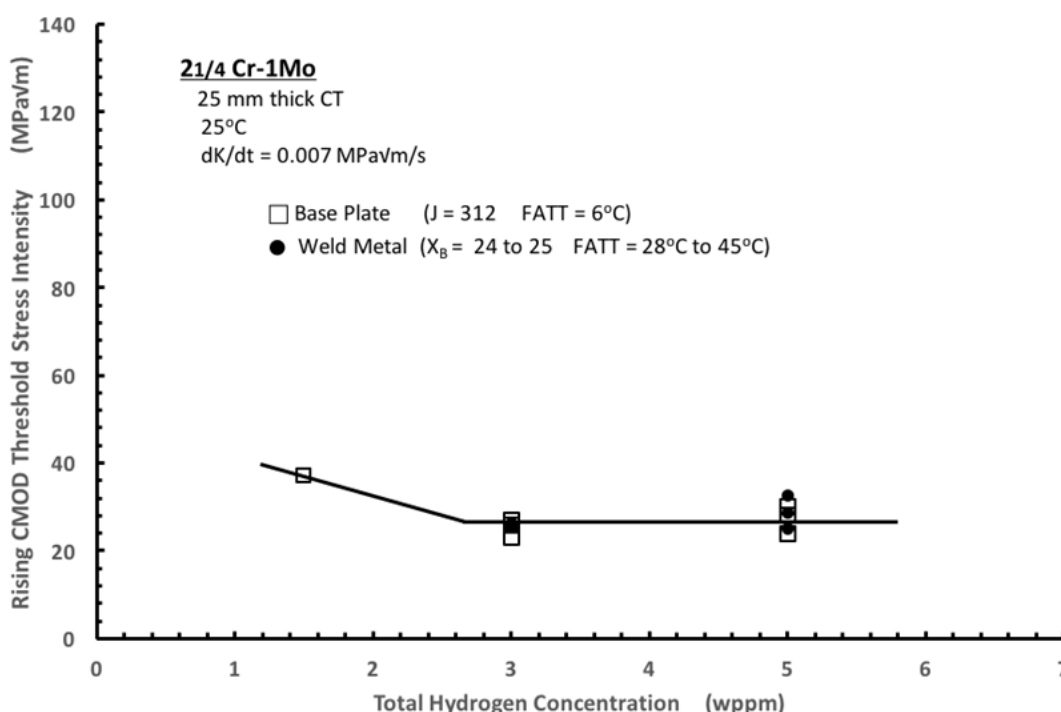


Figure 9—Effect of total-dissolved H concentration, produced by elevated temperature exposure in high-pressure H_2 , on the elastic K_{IH} for moderate purity (mid J and X_B) weld metal (step cooled $\text{FATT}_{\text{Thermal}} = 28^\circ\text{C}$ and 45°C)^[12,19] and base plate (step cooled $\text{FATT}_{\text{Thermal}} = 6^\circ\text{C}$)^[12] of $2\frac{1}{4}\text{Cr-1Mo}$ stressed in moist air at a single-slow-rising CMOD rate and 23 °C. These results contribute to Database B. ⁷

⁷ Iwadata, Nomura, and Watanabe established the dependence of K_{IH} on $\text{FATT}_{\text{Thermal}}$ for $2\frac{1}{4}\text{Cr-1Mo}$ base plate that was H precharged in H_2S bearing acetic acid solution providing a $C_{H\text{-Total}}$ of 2 wppm to 2.6 wppm. CT specimens were subjected to slow-rising CMOD at 25 °C.^[3,7] Their results are consistent with the H_2 -based data in Figure 9; for an $\text{FATT}_{\text{Thermal}}$ of 45 °C, $K_{IH} = 45 \text{ MPa}\sqrt{\text{m}}$. This K_{IH} value was defined at the first deviation from the H-free steel load-CMOD curve and is somewhat higher than the more precise data presented in Figure 8.^[3,11,3,12]