

The Technical Basis Document for API RP 941

API TECHNICAL REPORT 941-A
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Introduction

Addendum 1 to Technical Report (TR) 941-A, *The Technical Basis Document for RP 941*, First Edition, consists of Annex I and Annex J, and contains completely new information. (All pages prior to Annex I comprise the First Edition of TR 941-A). TR 941-A provides the technical basis for the Recommended Practice (RP) 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*, Eighth Edition.

Over the last several years, carbon steel equipment in the non-post-weld heat-treated (non-PWHT'd) condition has experienced cracking at conditions below the Nelson Curve for carbon steel published in the RP 941, Seventh Edition. Samples from the reported cracking incidents were examined at the University of Tennessee under the direction of Professor Carl Lundin to characterize the nature of cracking in an effort to determine if the cracking was the result of high-temperature hydrogen attack (HTHA). This work was performed in 2015 under the sponsorship of the API CRE Subcommittee on Corrosion & Materials (SCCM) 941 Task Group on HTHA.

The laboratory examination performed at the University of Tennessee is included as Annex J. It contains a detailed description of the examination and testing that was performed. This report suggests that several samples display traditional characteristics for HTHA, while others did not.

A second effort was initiated by the 941 Task Group to write this addendum as an update to TR 941-A, First Edition. The primary objective of this activity was to determine if the recently reported cracking incidents were the result of HTHA and whether the change to the carbon steel Nelson Curve appearing in RP 941, Eighth Edition is appropriate. Addendum 1 to TR 941-A has been completed and appears as Annex I and Annex J, as stated above. The conclusion reached by the 941 Task Group and conveyed in Addendum 1 is that the reported incidents of cracking of non-PWHT'd carbon steel were the result of HTHA and that these reported incidents justify the new curve for non-PWHT'd carbon steel appearing in RP 941, Eighth Edition.

Major findings conveyed in Addendum 1 are as follows.

- All but two of the samples of the reported incidents of cracking did not show visible signs of decarburization during metallographic examination of the observed cracking and fissuring. Currently, RP 941 states that decarburization occurs during HTHA as a result of carbide decomposition during HTHA. As part of the update to TR 941, First Edition, a material balance for the carbide (cementite) present in carbon steel was performed, indicating that it is possible that decarburization would not be observed when performing metallography of the fissured samples.
- Each reported cracking incident was examined and shown to possess characteristics expected for HTHA. In all cases, cracking predominately occurred along the boundary between pearlite and ferrite as expected for HTHA. The examination also indicated that welding residual stresses played a role in initiating and promoting through-wall cracking, especially in the cases where seamless piping or forged flanges displayed cracking.
- The observed through-wall cracking in non-PWHT'd equipment was very similar to cracking observed in carbon steel wedge opening loading (WOL) fracture test samples exposed to conditions that are expected to cause HTHA in carbon steel. This is discussed further in Addendum 1.

This completes the effort related to the examination of samples from the reported cracking incidents of non-PWHT'd carbon steel operating below the carbon steel Nelson Curve in RP 941, Seventh Edition. It was concluded that these cracking incidents were the result of HTHA and that it is appropriate to include them on the new Nelson Curve for non-PWHT'd carbon steel appearing in RP 941, Eighth Edition.

It is important to realize that the present effort is entirely based on the experience gained from examination of cracked samples removed from service. It is often difficult to determine the exact operating conditions these cracked samples were exposed to in service. As a result, there always is some uncertainty associated with establishing the exact condition for the Nelson Curves that appear in RP 941. This highlights our need as an industry to further study HTHA. At the present time, the industry is discussing various research proposals to model HTHA in an effort to develop more rigorously validated Nelson Curves. It is hoped that this effort will allow us to develop curves that are not subject to frequent changes based on observed cracking incidents from the field.

EXECUTIVE SUMMARY FOR THE TECHNICAL BASIS DOCUMENT

(From the 1st Edition, 2008)

Before the First Edition of API RP 941 “*Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*” appeared in 1970, there were fundamental questions regarding the technical basis for the materials performance curves contained in the document (1–6). Based upon sparse laboratory data combined with plant experience, with only a few exceptions, the curves have done an exceptionally good job at safely directing the refining industry in selecting materials based upon operating temperature, hydrogen partial pressure, and the metallurgy of the equipment being considered.

However, in some cases, past editions of API RP 941 were less successful, most notably for C-½Mo material. Today, with refining plants aging, engineers are seeking assurances that the curves are suitable for predicting continuing satisfactory performance for decades into the future. Of concern also, is the unusual shape of the 1 ¼Cr curve which appears inconsistent with the other curves without any obvious technical reason. Most important, engineers require technical justification for decisions made regarding suitability for service after process excursions that exceed the API RP 941 “safe” limits.

The API Committee on Refinery Equipment (CRE) Subcommittee on Corrosion and Materials (SCCM) commissioned the RP 941 Task Group to provide a technical basis document that goes beyond empirical evidence to address three issues:

1. Do the curves given in the current edition have the correct shapes and locations?
2. Are the curves likely to “change” with time as our plants become older?
3. What methodology and data can be used to handle process excursions?

The Task Group met these objectives.

The Technical Basis Document (TBD) that follows is the result of several years of effort incorporating the technical insights contributed by participating Japanese and European specialists with those presented to API from the United States. Dr. Martin Prager of The Materials Properties Council Inc. (MPC) prepared much of the TBD and developed the approach set forth in the main body of this document. Please see the acknowledgements of the contributions of the others noted below. Details can be found in the respective Annexes.

It is important in considering this work that it is a research report, not a recommended practice. Those workers most closely involved in this report believe some of the findings are so well supported that they can be immediately brought into the next edition of API RP 941. Examples are identified below. Other findings push the edge of our understanding and give very useful insight without yet being RP-ready. This is hard work, the complexity of which is matched by a frustrating lack of quality data in many cases. What goes into the next edition API RP 941 will be the work of the 941 Task Group.

Following are highlights of this document. For many, this level of detail, along with selected portions of the document to handle specific issues, will suffice. Those who delve into the entire document will be rewarded by Dr. Prager’s elegant explanations that bring us down to the mechanistic level, and back out again to provide guidance in dealing with actual plant challenges.

Highlights of the 2008 First Edition Technical Basis Document for API RP 941

- 1) The shapes and locations of the curves in the Sixth Edition of API RP 941 are essentially correct.
 - a) The carbon steel curve appears to be perhaps 30 °F to as much as 50 °F conservative. However, there is insufficient laboratory or plant data to justify adjusting the curve, and it is important to note that under special circumstances (e.g., unusually high stresses) there have been failures even below the current carbon steel curve.
 - b) All curves should have essentially the same shape. Therefore, the unusual “kink” in the 1 ¼Cr curve is likely incorrect. The API 941 Task Group should consider adjusting this curve.
 - c) The shape of the curves, where they go essentially “vertical” at low hydrogen partial pressures and become almost flat at high pressures, can be understood by taking into account kinetics, thermodynamics and materials’ strength. To a remarkable extent, attack quantitatively tracks the hydrogen and carbon solubility, which are low at low temperatures. Nevertheless, at low temperatures the methane pressure formed from even small concentrations of these elements can be enormous, much higher than the strength of the materials. Fortunately the kinetics is very slow at low temperatures, so that this full pressure is unlikely to be realized.
 - d) A key difference among alloys is actual carbon activity, which largely comes down to the amount of free carbon left in solid solution and that is in equilibrium with the carbides. The predominant carbide in carbon steel is cementite (Fe_3C). Cementite is the least stable carbide and when it is present, provides much of the easily reacted carbon. The relative stability of the carbides found in various alloys is discussed in this TBD.
- 2) We found no data or theory that would cause significant concern with equipment in hydrogen service operating below the current edition curve limits even for many hundreds of thousands of hours, as long as the equipment operates under code stress limits.
 - a) However, there is at least a theoretical concern that if the equipment is operated above the curve for that metallurgy, then hydrogen attack may initiate and possibly even continue after the operating conditions are returned to below the curve.
 - b) There is a theoretical basis for believing that for all practical purposes below certain conditions hydrogen attack will never occur.
- 3) The work found that the “incubation curves,” as given in the current and previous editions, are likely to be correct only for the specific set of conditions used to develop the curves. Yet we know that significant attack does not occur the instant material is exposed to conditions above the curves. An alternative approach for handling process excursions which is better founded on reaction rate and material strength principles is given in this report. Worked examples are given in Annex C of the report. Essentially:
 - a) High temperature hydrogen attack will not occur as long as the creep strength of the material is greater than the internal pressures caused by the buildup of methane.
 - b) The amount of methane pressure buildup in the steel depends upon the hydrogen pressure of the process, the temperature, and carbon activity in the material.
 - c) The greater the hydrogen pressure of the process, the more methane will be formed, but because at higher pressures, the gases no longer perform ideally, the attack becomes less sensitive to pressure and the curves tend to flatten at higher pressures. More importantly, the attack follows quantitatively the carbon and hydrogen availability in the material, and at lower temperatures the carbon and hydrogen solubility significantly decrease. Therefore, at lower temperatures, the hydrogen pressure must be greater to produce the destructive methane pressure in a given period of time.

- d) Higher temperatures will actually decrease the potential maximum methane pressure, but at the same time, higher temperatures reduce the creep resistance of the material and increase reaction rates.
- e) The material, and specifically the carbon and carbide content, is important. The greater free carbon that is available, the more methane pressure will build up for a set of operating conditions. A thermodynamically unstable carbide, such as Fe_3C , will actually worsen the situation by allowing more carbon to become available. Stable carbides, as found in low alloy material, provide markedly improved resistance by both reducing the amount of carbon available, and at the same time increasing the creep strength.
- f) Austenitic and even ferritic cladding dramatically reduces the effective hydrogen partial pressure behind the cladding, and can greatly retard or prevent HTHA. The attached report provides useful curves to easily predict the benefits of cladding. We believe this benefit is now well enough established that it should be recognized in the Seventh Edition of API RP 941.

Acknowledgements

The Task Group is particularly appreciative of the analysis and contributions of Dr. Tadamichi Sakai and Dr. Tohru Nomura who actively participated in Task Group meetings reporting on cooperative work funded by the Petroleum Energy Center of Japan through a Task group of the Japan Petroleum Institute. They built on work contributed by Japan Pressure Vessel Research Council as presented by Sakai and Nomura in Annex F. Also, the work of European investigators H. Van Wortel of TNO, S. Schlogl and E. Van der Geissen of TU Delft and T. Manolatis and A. Baker of JRC Petten as communicated to the Task Group by one member (R. Koers) was most enlightening and is contained in Annex G. Finally, Jay Cantwell's wealth of personal experience and insights gained in the refining industry (Annex A) provided an invaluable starting point.

E. H. (Ned) Niccolls

1.0 Abstract

Reports covering a half-century of comprehensive research on hydrogen attack have been reviewed. The major investigators were found to agree about what information would be needed to model the curves presented in API RP 941. However, they concluded that quantification of key, very complex material property and performance inputs is not possible. Prediction of attack limits from first principles, therefore, remains elusive. With the benefit of hindsight, the curves in API RP 941 are explained herein. A series of reasonable assumptions appear to justify Nelson's placement of the lines for carbon and low alloy steels.

The approach proposed here is applied to these common steels and agrees with trends in attack thresholds established by experience. It is based on the obvious and long-held notions that if the methane pressure in voids is low compared to the material's strength or methane forming reaction rates are low, attack does not occur. The approach is flexible and can be applied to all carbon and low alloy steels. It can also be used as a starting point to estimate the effect of applied stress on time-dependent behavior.

Application of these models to refinery equipment, especially clad components, has been attempted and the results are credible. Ferritic and austenitic stainless steel overlay and cladding are clearly effective. However, practical implementation of the principles is impeded by uncertainties regarding diffusivity, solubility, absorption rates, and fluxes of hydrogen and the effects of stress and materials strength.

Among the stumbling blocks to successful modeling of hydrogen attack is the lack of knowledge of relevant concentrations and activities of carbon and alloy elements remaining in solution after heat treatment. Also, there is scant knowledge of details about void nucleation and the rates of the methane forming reactions in voids. Local compositions at grain boundaries and the compositions of carbides are probably important, but are not known with certainty. The manner and rate of the evolution of hydrogen attack damage have not been studied quantitatively.

Prediction of attack boundaries is difficult since materials of a grade differ in critical respects and those that have been attacked in service have never been fully characterized (as discussed in Annex A). Systematic laboratory studies of the effects of heat treatment and stress could build confidence in the conclusions offered here and provide valuable information for life assessment and risk evaluation.

2.0 Introduction

High temperature hydrogen attack (HTHA) considered here is the appearance of voids or cracks containing methane at grain boundaries and inclusions of some steels when they are exposed to hydrogen environments. It occurs in carbon and low alloy steels at temperatures above at least 400 °F because carbon and carbides in the steel may react with dissolved hydrogen to form the non-diffusible hydrocarbon gas. The rate of formation of methane is expected to depend on the temperature, amount of hydrogen dissolved in the steel, and many metallurgical factors, especially the thermodynamic activity and concentration of carbon in solution.

HTHA was first reported about 75 years ago (7), but is not yet adequately understood. It causes concern and occasional failures in the refining, chemical, and power industries. The purpose of this report is to offer a technical basis for the pressure-temperature operating limits provided by API RP 941 for equipment in petroleum industry hydrogen service. Conservative guidance in API RP 941 has been drawn mainly from reports of experience as described in Annex A. In contrast, there has been little acceptance by industry of quantitative pressure-temperature

attack limits developed from first principles by researchers, nor has there been progress on remaining life estimation tools for possibly damaged steel.

This report includes the positions of researchers in Japan, Europe, and America as recently communicated to the API 941 Task Group. Included herein is an overview of concepts that have been used over the years to understand the technical basis for operating limit curves of API RP 941. These concepts range from explanations based on extrapolation of simple exposure experiments to finite element models of the complex phenomena leading to void growth and cracking. Despite the efforts of dozens of researchers over the last 30 years, there has not been a successful and widely accepted synthesis of observations with the models for HTHA. The basic shapes of the curves can be justified, but their locations and the effects of applied stresses have not been adequately rationalized.

Occasional problems with C- $\frac{1}{2}$ Mo steel in long term service below the published limits for the alloy have raised concerns about the guidance found in API RP 941 with regard to other steels. For example, the question has been asked “Does resistance to HTHA decrease during time in service (as a result of aging)”. Before that question and others noted below can be answered, it is essential to see where we are regarding the fundamentals of hydrogen attack and the evolution of damage. Some further details and barriers to understanding behavior and future directions for needed studies are indicated in Annex B and Annex E. It should be noted at this point that the frequent references to C- $\frac{1}{2}$ Mo steel in this document should be viewed as applying to Mn- $\frac{1}{2}$ Mo steels and steels of similar composition. The current state of firm knowledge does not permit drawing fine distinctions with regard to elements that are not strong carbide formers.

Based on this review of research, a semi-quantitative technical basis is offered for the current pressure-temperature curves and computing time to failure under the combined effects of hydrogen pressure and stress. These principles should be refined so they might be applied to handle excursions above the Nelson Curves as described in Annex C and Annex H (the latter prepared by the API 941 Task Group).

The mounting body of evidence that the C- $\frac{1}{2}$ Mo steel lines proposed by Nelson were inappropriate (Annex A) stimulated interest in developing a technical basis for establishing recommended safe operating boundaries for carbon and low alloy steels in high temperature hydrogen service. Among the questions about why Nelson’s curves for C- $\frac{1}{2}$ Mo steel needed to be repeatedly changed were the following: (Note that, today, some engineers are asking the same questions about 1Cr- $\frac{1}{2}$ Mo and 1 $\frac{1}{4}$ Cr- $\frac{1}{2}$ Mo- Si steels.)

- 1) Were operating conditions reported to Nelson correct?
- 2) Were the lines incorrectly drawn?
- 3) Did the materials that displayed attack in service change in time so they became increasingly susceptible to attack over many years?
- 4) Is there an incubation period after which attack is rapid?
- 5) Did attack proceed from the start of exposure, but methods of detection were too insensitive to disclose the progress of damage?
- 6) What role is played by corrosion products or cladding in impeding hydrogen entry into the steel and subsequent hydrogen attack?
- 7) How might one do a Fitness-for-Service evaluation?

To address these questions and more, an examination of public domain information and relevant research has been accomplished. Researchers in Japan and Europe were enlisted in a cooperative effort under the API program.

Much of the discussion about published laboratory test results was accompanied by what seemed at the time to be very reasonable supposition and conjecture, but which has not stood the test of time. The utility of information from operating plants is not useful in many cases because of inadequate descriptions of the exposure conditions, materials studied and degree of attack. The author has tried to separate facts from conjecture. However, fully satisfactory answers to the when and where of attack cannot be provided because of the limited reliable information available, the complexity of the phenomenon and the many variables that play a role. What follows instead are current positions, some practical tools and suggestions for resolving the areas of ignorance. This is done in the hope that this work will form the basis of a better directed experimental program to get the additional information that engineers need.

2.1 What is Hydrogen Attack?

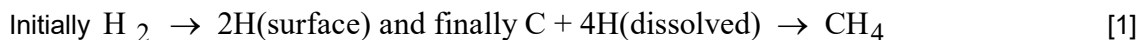
API RP 941 recognizes two basic types of hydrogen attack:

- 1) Reactions on surfaces exposed to the process stream and evidenced by decarburization.
- 2) Internal damage as evidenced by voids (“bubbles”), cracks, (micro) fissures and blisters, sometimes associated with internal decarburization.

Both types of attack derive from the reaction of carbon or carbides with hydrogen to form methane. Methane formed at the surface escapes and the decarburization usually does no significant damage to the load carrying capability of the component. Methane formed internally is trapped since molecules of methane cannot diffuse through steel. This internal attack is of primary concern here.

Methane pressures at the site of internal attack can build to high levels forming or growing voids or cracks. The steel may then suffer progressive internal ruptures which reduce strength and toughness. With time, the depth at which methane appears may increase and the damage may propagate through the thickness, well beyond the surface exposed to the hydrogen. If undetected, cracks in stressed components may grow to failure. Weakened, fissured material may fail on startup due to loss of tensile strength or inadequate toughness. [Figure 1](#) to [Figure 5](#) indicates the key features of internal HTHA.

A simple and thermodynamically correct way to view HTHA, even for steels with complex carbides is to consider the behavior of hydrogen and carbon in the steel (8–16). Then the reactions may be expressed as follows:



The thermodynamic driving force for the methane reaction, the negative free energy change for Equation [1], increasingly favors methane formation with decreasing temperature as shown in [Figure 6](#).

As described below, calculations show that the internal pressure that may be produced by the trapped methane can exceed the nominal tensile or creep strength of the steel at the reaction temperature, even for low concentrations of carbon and hydrogen in the steel. Fortunately, the kinetics of the reaction slows with decreasing temperature and we expect an apparent threshold temperature for each steel, below which the attack rate is negligible.

Because of the high availability of carbon in carbon steels and the carbon 0.5% Mo type alloy steels, reactions may proceed at significant rates even at low temperatures provided hydrogen pressure (and therefore solubility) is high. Materials rich in carbide-forming elements (low carbon concentration and activity) can be used at high temperatures and pressures. [Figure 7](#)

shows how this consideration results in comparable reaction rates for the various classes of materials found in API RP 941 in their respective correct ranges of temperatures and pressures ([Figure 8](#)).

Thus, it is concluded that, for each alloy considered in API RP 941, reaction kinetics govern the pressures at which attack is observed in the lower temperature regime and the pressure at any temperature depends on carbon availability.

The free energy of methane formation for reaction [1], above, is related to the pressures or activities of the participating species as follows:

$$\frac{F_{CH_4}}{P_{H_2}^2 a_c} = e^{\frac{-\Delta G}{RT}} = K_{eq} \quad [2]$$

Where the terms are defined as follows:

$F_{CH_4} =$	Thermodynamic effective “pressure” called the fugacity of methane. Methane is a very non-ideal gas at the pressures of interest. Therefore, fugacity, not pressure, is used for the calculation. The actual pressure of methane formed may be much lower than the fugacity, but may be very high relative to the creep or even tensile strength of the steel.
$P_{H_2} =$	Partial pressure of hydrogen. It is assumed hydrogen behaves as an ideal gas, so pressure may be used in the calculation. Also, for the calculation, it is assumed that the hydrogen pressure in the gas and the solubility in the solid are related through Sievert’s Law, i.e. concentration is proportional to the square root of the partial pressure in the environment. <i>Note the frequent references in this report and figures herein to hydrogen pressures or partial pressures in psi units should be taken to mean psia.</i>
$a_C =$	Activity of carbon in solid solution and in equilibrium with carbides in the metal. The value to use is for carbon dissolved in the iron matrix in contact with the <u>least</u> stable carbide phase in the steel. For alloys rich in carbide formers, such as molybdenum and chromium, a number for the activity much smaller than unity may be correct, say 0.01 to 0.1 when referred to graphite as carbon’s standard state where activity is equal to 1. Where carbide formers are not plentiful and Fe_3C, cementite, predominates, the effective activity (relative to graphite) may be viewed as greater than 1 since Fe_3C is metastable (not an equilibrium phase) and ΔG numerically exceeds that for the graphite reaction. The values of carbon activity in equilibrium with mixed (alloyed) carbides in low alloy steels have been calculated by many researchers. While they are probably accurate, the results are only approximately confirmed. This is because it is not convenient (or even understood how) to practically measure the activity of carbon in a solid alloy. Additionally, the actual activity of carbon in solution depends on heat treatment, temperature, and time. Equilibrium may not be reached and use of the equilibrium calculated value may not be appropriate. Unfortunately, the value of carbon activity chosen significantly affects the estimate of the most important driving force for HTHA, the methane pressure. If the least stable carbide is one of vanadium, molybdenum or chromium, the methane fugacity and potential pressure are greatly reduced as indicated by the above equation and discussed later.
$\Delta G =$	Free energy of formation for methane. If calculated on the basis of a reaction with cementite, the magnitude of the free energy change increases significantly over that calculated using graphite as carbon’s standard state. The potential methane partial pressure can be very large.
$K_{eq} =$	Equilibrium constant
R and T have the usual meanings in any units consistent with those used for ΔG .	

A brief discussion of the role of kinetics on HTHA may be helpful here. Among the reactions possible leading to the formation of methane in steel are the following, where (ad) suggests that the reaction takes place on a metal surface, external or in an internal void (cavity):



Allen, et al. (17) proposed that the rate of methane formation should be proportional to the fourth power of hydrogen content multiplied by the carbon content. This is reasonable from ordinary reaction rate theory, although a lower exponent for the concentration dependence is possible, as might be indicated by Equation [3] through Equation [10] above. Few details of the reactions in steel are known.

Grabke and Martin (18) experimentally determined the kinetics, the rate of formation and decomposition of methane during decarburization at an iron surface. If one assumes that the basic processes are similar to what would happen in a void and if dn_c/dt denotes the rate of change in the number of moles of carbon in the metal, Grabke's and Martin's results are:

$$\frac{dn_c}{dt} = -A \left(K_1 C_m P_{\text{H}_2}^{3/2} - K_2 F_{\text{CH}_4} / P_{\text{H}_2}^{1/2} \right) \quad [11]$$

where:

A is the surface area of involved,

K_1 is the forward reaction constant for formation,

C_m is the carbon concentration at the surface in moles-cm⁻³,

K_2 is the reverse reaction constant,

F_{CH_4} and P_{H_2} are the fugacity and pressure of methane and hydrogen respectively in atmospheres.

The values of K_1 and K_2 measured by Grabke and Martin were:

$$K_1 = 1.64 \times 10^{-1} \exp(-13.6 \text{ kcal}/RT) \text{ cm}^{-1} \text{ sec}^{-1} \text{ MPa}^{-3/2} \quad [12]$$

$$K_2 = 4.1 \times 10^3 \exp(-51.0 \text{ kcal}/RT) \text{ cm}^{-2} \text{ sec}^{-1} \text{ MPa}^{1/2} \quad [13]$$

These rate constants were obtained for pressures around atmospheric, but lacking other data, we assume that they can be applied at the pressures within voids as considered here.

There are many impediments to applying these equations, but since the intent here is to roughly identify the boundaries where reaction rates may govern, the magnitudes and trends indicated should be explored. The forward reaction, Equation [12], is of particular interest. Logically, the reverse reaction Equation [13] should not be of concern unless significant methane pressure has built up in the steel, so it need not be considered in determining when conditions are amenable to production of methane.

There are three variables of concern here—temperature, pressure, and carbon content (related to carbon activity and the precipitated carbides). Calculations using the above equations show that the forward reaction starts to increase rapidly at high pressures in the neighborhood of the temperatures we see for hydrogen attack limits in API RP 941 for carbon steels, as shown in [Figure 8](#). Attack rates are equally rapid at low pressures only at high temperatures for steels with high carbon activity. In order to achieve sufficient reaction rate where carbon activity (dissolved carbon) is low, as in steel containing strong carbide forming alloying elements, the temperature and pressure must be high enough that sufficient hydrogen may be dissolved in order to compensate for the lack of availability of carbon. This concept does not need to deal yet with the number of sites at which the reaction can occur. Low energy interfaces, inclusions, coarse carbides, and other heterogeneities of the microstructure will influence relative susceptibility to attack. The point is that if the driving force and the rate are insufficient, attack will not occur. Above the minimum pressure-temperature limits, relative rates are of concern. Annex C deals with some additional aspects of the rate question.

Finally, in support of this rate limitation concept, it is obvious that the methane reaction and/or cavity nucleation rates must be very slow at low temperatures, given the potentially high methane pressures that could be generated, given the increasingly large thermodynamic free energy change of the reaction with decreasing temperatures. Otherwise, attack would occur in common equipment operating at low temperatures, even at low hydrogen pressures

2.2 What Fugacity is and Why it is Important

Methane does not behave as an ideal gas. As a result, the partial pressure of methane that can be developed in the steel is lower than the fugacity defined above. The fugacity-pressure relation of methane was reported about 25 years ago and is widely accepted by all investigators (8, 19, 20). It can be cumbersome to implement. For convenience, the approach adopted in the following text is based on an approximation that introduces very little error over the entire range of temperatures and hydrogen pressures of interest. [Figure 10A](#) presents the relation used here, i.e.:

$$F_{CH4} = P_{CH4} e^{\beta P_{CH4}} \quad [14]$$

Strictly speaking, β is a function of T and P_{CH4} (see Annex F and Annex G for a more lengthy discussion). However, when β is an appropriately chosen constant, errors introduced in the calculated methane pressure, over the range of temperatures and pressures of interest, are small. They are also irrelevant, since we do not expect that equilibrium will be reached (nor would we know it, if it were) and there are many other, larger uncertainties in the calculations that must be made.

The equation shown above cannot be conveniently solved for P_{CH_4} when F_{CH_4} is specified since the variable, P_{CH_4} , cannot be usefully mathematically separated in Equation [14]. An iterative solution must be used. When β is a constant, the iteration is simplified.

The non-ideal gas behavior of methane was not understood when many experiments were planned by early researchers (17, 21–24). As a result, the data obtained could not be properly interpreted. This slowed progress in understanding HTHA.

The equilibrium methane pressure increases with carbon activity (see [Figure 10B](#)). The values of P_{CH_4} possible were always recognized to be of the magnitude of the tensile or creep strengths of the materials of interest.

Caution: The units of β and P must be consistent. A value of 0.005 for β applies when P_{CH_4} is in MPa and is usually the value shown in the literature. As noted above, the “constant”, 0.005, in the fugacity equation is not strictly correct for all methane pressures and temperatures. Changes of β at very high methane pressures lead to noticeable differences in the fugacity estimates. The converse is not true. Estimates of methane pressure for a given fugacity are relatively insensitive to the value of β used. A sensitivity study by the author over the range of fugacity values of interest showed the error in estimating methane pressure will not exceed about 5%. Therefore, 0.005 was used exclusively in this work.

The units of P_{CH_4} in the pre-exponential term in the above equation must be consistent with those used for fugacity. Since, the equilibrium constant is calculated with the units of fugacity, atmospheres, methane pressure in the pre-exponential term must then be expressed in atmospheres when hydrogen pressure is also in atmospheres. Methane pressure is converted and expressed in ksi in this report for ease of discussing mechanical properties in the USA.

2.3 Details of the Attack Progression

2.3.1 Solubility

Before discussing theories, data, and mechanisms, and attempting to predict of safe operating limits, a brief discussion of what occurs during void and crack formation may be helpful. On exposure to hydrogen at elevated temperature and pressure, hydrogen will be first adsorbed and then (absorbed) dissolved in the steel. (Equation [3] and Equation [4]) The limiting (maximum) amount of hydrogen that can be dissolved in carbon and low alloy steels is calculated from an equation of the form:

$$C_H = Ae^{-Q/RT} P_{H_2}^{1/2} \quad [15]$$

where:

A = a constant, and

P_{H_2} = the hydrogen (partial) pressure, and

Q = an activation energy.

This is Sievert's Law. Typical values of the solubility may be seen in [Figure 11](#) based on a set of constants in [Table 1](#) used over many years in API publications. It should be noted that the amount of hydrogen dissolved in steel under attack conditions is very low, only a few parts per million (ppm) by weight, at most, as may be judged from [Figure 11](#) and [Figure 12](#). For carbon steel and C-½Mo steel, the dissolved hydrogen content under attack conditions appears to be on the order of 1 ppm by weight or less ([Figure 12](#)). It is several times higher in low alloy steels where carbon activity is much lower.

Lines of constant solubility in T–P space ([Figure 12](#)) bear remarkable similarity to some of Nelson's curves. They suggest that the attack limits may be related closely to the amount of hydrogen dissolved. Again, in the case of carbon and the 0.5% Mo steel, only about 1 ppm provides a sufficient driving force and rate at the temperatures of interest.

Values of the constants *A* and *Q* should depend on alloy content, carbon content and heat treatment (microstructure). Data for the specific piece of steel used in a refinery application are never available. The solubility of interest for calculating the rate of hydrogen attack is the dissolved, atomic hydrogen content. Measurements of hydrogen solubility are rendered difficult by trapping of H₂ molecules at microstructural defects, carbide interfaces and imperfections in steel. [Table 1](#) indicates the range of uncertainty when assigning values to hydrogen solubility in steel based on various data in the literature. Depending on how hydrogen content is measured some of it may be associated with trapped hydrogen molecules. A sound wrought steel product not previously exposed to a hydrogen atmosphere may contain trapped, molecular hydrogen exceeding 1 ppm by weight. The amount is a function of the melting practice, microstructure and processing. After exposure to a hydrogen containing environment, the amount trapped may be several ppm.

Table 1—Solubility Ranges Calculated, Micromoles per Cm³ at Indicated Temperature, °F, Reported for Low Alloy Steels

Temperature	400	450	500	550	600	650	700	750	800
Low Values	0.56	0.81	1.14	1.54	2.03	2.61	3.28	4.04	4.90
High Values	1.15	1.68	2.34	3.17	4.17	5.36	6.73	8.29	10.05

Assuming a void volume in the material of 1×10^{-2} percent, (i.e. 99.99 theoretical density) and a trapped molecular hydrogen content of 1 ppm, we can calculate the possible pressure of hydrogen in voids as follows (assuming it does not dissociate and dissolve first):

1 ppm of hydrogen by weight is:

$$7.8 \times 10^{-6} \text{ g/cm}^3 \text{ or } 3.9 \times 10^{-6} \text{ moles H}_2/\text{cm}^3 \quad [16]$$

The volume of that mass at normal or standard conditions of temperature and pressure is:

$$[(3.9 \times 22.4 \times 10^3 \times 10^{-6}) = .085 \frac{\text{cm}^3 \text{H}_2}{\text{cm}^3}] \quad [17]$$

The corresponding hydrogen pressure at 10^{-2} void percent would be in the ratio of the amount in Equation [17] to 10^{-4} or on the order of 850 atm or 12,500 psi at ambient temperature. At operating temperatures for refinery equipment, the pressure of molecular hydrogen in the void would be about twice as high. The reaction to form methane would at first reduce the pressure (also some hydrogen would dissolve in the surrounding steel). Complete conversion to methane without further inflow of hydrogen would reduce the pressure by about a factor of two. At

temperatures where the reaction rate is rapid and strength is low, trapping sites or voids might be natural HTHA nucleation sites. However, 1 ppm of hydrogen would consume only 3 ppm of carbon. The methane forming reaction must continue and use more than 100 times as much carbon for swelling, void growth and eventual local internal decarburization. However, such voids or interfaces are reasonable sites for initiation of methane reactions. Where such nuclei are numerous, attack may be manifested relatively quickly and continue where sufficient hydrogen is available.

2.3.2 Incubation Times

The availability of easy nucleation sites is pertinent to the question of an incubation time for hydrogen attack. Investigators studying carbon and 2 ¼Cr-1Mo steels have shown that swelling occurs almost immediately on exposure to conditions favorable for hydrogen attack. The experiments of McKimpson and Shewmon (25), for example, disclosed immediate expansion. The widespread notion of an incubation period during which there is no attack may be attributed to the fact that in the early stages of attack voids are extremely small—only a fraction of a micron—and go undetected, using even the best optical microscopic techniques.

API RP 941 refers to a period of no noticeable attack as the incubation period. Clearly, the duration of that period is dependent on the means of detection. As the years have passed, the means of detection have improved. Now, the original incubation curves should be viewed as the conditions for detection of attack in specific steels, rather than a threshold time for attack in an alloy grade. Given the variability of carbon and 0.5% Mo steels, it should be appreciated that some components may suffer severe attack or even failure in the time periods noted in API RP 941, while others might evidence little or no attack when studied over much longer periods of time, even using sensitive Metallographic methods.

For this review, McKimpson's (25) expansion rate data for carbon steels at various pressures and temperatures have been reanalyzed using the thermodynamically predicted equilibrium methane pressure as the driving force. This exercise suggested the usefulness of methane pressure as a key variable for predicting attack. (Many had suggested this in the past, but had not followed through due to uncertainty about the calculation or strength parameters). The equation now found for McKimpson's data with a R^2 of 0.95 on the log of expansion rate was:

$$\log \text{ expansion rate} = .88448 - \frac{21659.1}{T} + 2.268 \log P_{\text{CH}_4} \quad [18]$$

The low exponent (i.e. 2.268) for the methane pressure dependence is not inconsistent with current void growth models. (In Annex G, a more complete discussion of values is provided and it would appear that the value should may depend on the alloy and temperature or even population and distribution of nuclei).

McKimpson reported that after a period of relatively constant rate, the expansion rate increased exponentially. This is sensible. As voids grow, additional nuclei are generated in the immediate neighborhood because of the local stresses around the voids and the expansion rate accelerates.

2.3.3 Growth of Cavities

In the usual general approach, the growth rate of voids is divided into a volumetric growth rate due to the diffusion of atoms into the grain boundary, $\dot{V}_{\text{diff}}^{\text{cav}}$, and a contribution resulting from creep flow in the adjacent grains, $\dot{V}_{\text{cr}}^{\text{cav}}$:

$$\dot{V}^{\text{cav}} = \dot{V}_{\text{diff}}^{\text{cav}} + \dot{V}_{\text{cr}}^{\text{cav}} \quad [19]$$

The two contributions depend on the cavity geometry and the driving stresses for void growth.

For HTHA, the pressure p_m inside the cavity is usually set as

$$p_m = p_{\text{CH}_4} + p_{\text{H}_2} \quad [20]$$

and it is the dominant driving force. More recently, investigators account for the influence of additional stresses resulting from applied loading.

The volumetric growth rate due to diffusion is given by

$$\dot{V}_{\text{diff}}^{\text{cav}} = 4\pi\mathcal{D} \frac{p_m - (1-f)2\gamma_s \sin \psi / a - f2T_s \sin \psi / a}{\ln(1/f) - \frac{1}{2}(3-f)(1-f)} \quad [21]$$

with f = a function of cavity size and spacing

Here, $\mathcal{D}$ is a temperature dependent diffusion parameter, defined by $\mathcal{D} = D_B \delta_B \Omega / kT$ in terms of the boundary diffusivity $D_B \delta_B$ and the atomic volume Ω . For further details see Annex F and Annex G. The expression in Equation [21] can account for the effects of surface energy γ_s and the surface tension T_s , and ψ is the surface angle describing the cavity as represented in [Figure 2](#).

The creep contribution $\dot{V}_{\text{cr}}^{\text{cav}}$ is taken to describe the growth of a hole in an incompressible power-law creeping solid subjected to a uniaxial tensile stress, σ . The growth of a cavity by creep depends strongly on the stress triaxiality. In the case of purely hydrostatic internal methane plus hydrogen pressure p_m (corrected for the surface tension T_s as shown below) the volumetric growth rate expression sometimes used is:

$$\dot{V}_{\text{cr}}^{\text{cav}} = 2\pi\dot{\epsilon}_m a^3 h(\psi) \text{sign}(\sigma_m) \left[\frac{1}{1 - (0.87a/b)^{3/n}} \alpha_n \right]^n \quad [22]$$

with

$$\sigma_m = p_m - 2T_s \sin \psi / a, \quad \dot{\epsilon}_m = B\sigma_m^n, \quad \alpha_n = 3/(2n). \quad [23]$$

The relative contributions of diffusion and creep to void growth are weighted through a mathematical parameter with the dimension of length.

$$L_m = [\mathcal{D} p_m / \dot{\epsilon}_m]^{1/3}. \quad [24]$$

Large values of L_m compared to, for instance, the cavity spacing b , indicate that growth is dominated by diffusion, while smaller values indicate increasing contributions by creep deformation.

Most modelers assume that nucleation of the cavities takes place at the beginning of the HTHA process over a time that is much shorter than the total lifetime. Hence, the half cavity spacing b is taken as a constant. Given the hydrogen and methane pressure and the cavity size, one can compute the instantaneous growth rate of a cavity by substitution in the volumetric growth rate expressions. The complete attack evolution is obtained by time step integration until a critical value of a/b is reached at which time cavity coalescence takes place (sometimes taken to be $a/b = 0.7$). Annex G presents an overview of the most recent modeling of the growth behavior. While this approach provides an elegant picture of behavior, it has not been quantitatively successful because of the large number of assumptions and terms needed for prediction. Additionally, there is scant data on how diffusion, creep, damage, and continuous nucleation interact in reality. The sensitivity to nuclei size, spacing and continuing nucleation is great. Thus, these are elegant models with acknowledged limited predictive capabilities.

2.3.4 Hydrogen Diffusion

The maximum hydrogen contents shown in [Figure 11](#) and [Figure 12](#) were based on reaching equilibrium solubility as calculated using published values of Sievert's law constants. Equilibrium with the gaseous or liquid phase in contact with the solid may not occur if diffusion away from the exposed surface is rapid or ingress is retarded. Rates of absorption from the process stream and diffusion away from the surface determine the actual hydrogen content. Assuming the hydrogen content at the remote surface is zero, the flux, F , is:

$$F = DC_H / t \quad [25]$$

where:

D = Diffusivity,

C_H = hydrogen content of steel in contact with the gas phase and

t = thickness

and

$$D = A_D e^{-Q_D / RT} \quad [26]$$

The literature provides a wide range of values for diffusivity and associated activation energies. As shown in International Institute of Welding (IIW) surveys (26, 27), [Figure 13](#) through [Figure 17](#), diffusivity of hydrogen in steel depends on microstructure, alloy content and temperature. High values of diffusivity suggest proportionally greater thickness at which theoretical, maximum concentrations may not be achieved for a given flux. The range of uncertainty in diffusivity estimates is even greater than for solubility. Where diffusivity is high or adsorption rate low or impeded by a surface coating, a thin-wall component may have a lower hydrogen content than predicted by Sievert's law and will be at greatly reduced risk. This is because as described earlier, both methane pressure and reaction rate vary with the hydrogen concentration raised to a power. The net result is virtual elimination of the possibility of attack where hydrogen content

is suppressed. The most important example of this is the application of clad or overlay on the ferritic steel surface as described below.

2.3.5 Hydrogen Entry into the Steel—The Role of Clad or Overlay

Impeding ingress of hydrogen into the metal lowers the hydrogen concentration and lowers effective or equivalent hydrogen pressure calculated by substituting the actual concentration into Sievert's equation.

Austenitic stainless cladding is well known as a hydrogen barrier (28, 29). Ferritic stainless steels are also effective as illustrated in [Figure 18](#) and [Figure 19](#). Corrosion products may be similarly beneficial. The mathematics of dealing with corrosion products is not obvious, since thickness, hydrogen solubility and diffusivity are not measured or recognized as properties of the corrosion product layer. However, a corrosion product may be treated as an equivalent or added thickness of cladding. As described in Annex D, a coefficient γ obtained from measurement of the flux change associated with a corrosion product can be used to account for the presence of the corrosion product and used to estimate the backing steel concentration and equivalent hydrogen pressure. These equations, similar in form and function to those used to relate the effective hydrogen pressure under cladding or overlay and flux and hydrogen concentration can be used to account for the effects of corrosion products in a range of situations. Annex D provides the basis for equations for calculating effective pressures in the backing steel and a diagram helpful in understanding the terms used.

The terms used are as follows;

F_C, F_{CP}	=	Hydrogen flux associated with clad or corrosion covered component, respectively.
P_E	=	Hydrogen partial pressure in operating environment.
P_C	=	Hydrogen effective pressure at the clad/overlay surface closest to environment.
P_B	=	Hydrogen effective pressure at the backing steel interface closest to environment.
D_C, D_B	=	Diffusivities of hydrogen in clad/overlay and backing steel, respectively.
X_C, X_B	=	Thicknesses of clad/overlay and backing steel, respectively.
C_C, C_B	=	Solubility of hydrogen in clad/overlay and backing steel at 1 psi hydrogen partial pressure, respectively. Terms are dependent on temperature and expressed in appropriate units.
R_C	=	Pressure reduction ratio at backing steel interface due to presence of clad/overlay, i.e. P_B / P_E
R_{CP}	=	Pressure reduction ratio at steel interface in the presence of corrosion product, i.e., P_B / P_E in corrosion situations
ξ	=	Coefficient used to relate flux to pressure differential for corrosion product. Assumed independent of temperature and pressure.

Then, for clad material:

$$P_B^{1/2} = \frac{P_\varepsilon^{1/2}}{\left(1 + \frac{D_B C_B X_C}{D_C C_C X_B}\right)} \quad [27]$$

Where P_B is the effective hydrogen pressure at the bond line and P_ε is the hydrogen pressure in the process stream.

$$\text{Setting } \frac{D_B C_B X_C}{D_C C_C X_B} = Z \quad [28]$$

Where D , C , and X are diffusivity, concentration and thickness and subscripts. B and C refer to backing steel and clad/overlay, respectively.

For clad with corrosion product (say sulfides) on the clad surface:

$$P_B^{1/2} = \frac{P_\varepsilon^{1/2}}{\left[1 + \frac{D_C C_C}{X_C \xi} \left(\frac{Z}{1+Z}\right)\right] (1+Z)} \quad [29]$$

It can be seen from [Figure 20](#) and [Figure 21](#) that the benefit (reduction effective hydrogen pressure) of a corrosion product and/or cladding (overlay) is dependent on the relative thickness of overlay and backing steel and temperature.

For ferritic (400 series, 9–12 chrome), clad or overlay, the relevant product of diffusivity and solubility is reported to decrease with increasing chromium contents up to about 15% by about a factor of 4, compared with carbon steel (30). This compares favorably with austenitic stainless steels where the product is usually taken to be about 10. This indicates that high-chromium ferritic clad/overlay can impart appreciable benefits to low alloy steels now in refinery service.

The reductions in hydrogen pressure associated with a broad range of practical clad/ or overlay/backing steel thickness combinations are shown in [Figure 20](#) and [Figure 21](#). It can be seen that for thin components, the effect is dramatic and would explain optimism about C-½Mo steel if the experience with clad components is included with the input data in Nelson's plots without adjusting for the reduction in hydrogen pressure in the backing steel interface.

3.0 Attack of Materials Containing Fe₃C

Carbon steels and C-½Mo steels, may contain significant amounts of cementite (Fe₃C or M₃C in low alloy steels). Every metallurgist is taught that cementite is not thermodynamically stable relative to its components, iron and carbon (graphite), i.e. the free energy of formation of cementite is greater than zero. The consequence of that fact with regard to HTHA is that the pressure resulting from methane formation in the vicinity of cementite is higher than if carbon were in a solid solution containing more stable carbides or even graphite. Another way to look at the situation is that the activity of carbon in ferrite with cementite may be viewed as though it is greater than one, in comparison to the free energy change based on methane from graphite. Calculating the methane pressure using the free energy of formation from pure cementite, a carbon activity of one is appropriate. Alloying of cementite with molybdenum, chromium or other

slightly soluble carbide formers reduces the free energy of formation of methane and carbon activity can be reduced accordingly, depending on the degree of enrichment with the elements cited. [Figure 22](#) shows the difference in the free energy change for methane from graphite and from cementite.

Using the free energy of formation for the metastable Fe_3C phase, the equilibrium methane pressure calculated in accordance with Equation [2] is higher than when the calculation is based on the reaction of carbon (graphite) dissolved in iron. Methane pressures for hydrogen in equilibrium with pure Fe_3C at temperatures of interest here are shown in [Figure 23](#).

From [Figure 23](#), it is obvious that at the equilibrium methane pressure calculated can exceed the tensile strengths of carbon and C-1/2Mo steels at these potential operating conditions, even at low hydrogen pressures. The fact that steel is commonly used with hydrogen at lower temperatures must mean equilibrium is not achieved, i.e. nucleation of cavities does not occur and/or the rate of the methane forming reaction is negligibly slow. As a result high-pressure equipment can be successfully operated at temperatures below those shown in [Figure 23](#). Because of the non-ideal gas (fugacity relationship) for the behavior of methane described earlier, at low temperatures the equilibrium methane pressure in contact with cementite is relatively insensitive to hydrogen pressure ([Figure 23](#)). However, this insensitivity does not explain the flatness of Nelson's P/T curves at low temperatures with increasing pressure. The potential methane pressures at low temperatures are so unrealistically high, they can never occur. Failure would be expected at even low hydrogen partial pressures. Instead, the explanation involving kinetics offered earlier is the most plausible and consistent for the flat disposition of the low temperature portions of each of Nelson's curves indicating tolerance for very high hydrogen pressures below a threshold temperature range.

In regard to the steeply rising portions of the curves, investigators initially speculated that methane pressure was the driving force for cracking, but they had no way of quantifying the pressure and time dependencies of attack. Now, methane pressure can be shown to correlate with the time dependent (isochronous) carbon steel and other attack lines shown in API RP 941 ([Figure 24](#) and [Figure 25](#)).

While not describing any particular material, the carbon steel lines may be valid indicators of the correct trends of laboratory data for the materials reported to Nelson. A plot of reciprocal temperature and methane pressure for each of the times is shown in [Figure 25](#). The calculations upon which these curves were based used the free energy of methane formation from unalloyed Fe_3C . The standard state for each reactant in the equation was set at unit activity (H_2 and Fe_3C) to calculate methane fugacity and then its pressure.

The roughly linear dependence with methane pressure observed over the range of temperatures of interest suggests a possible important role of methane pressure in the kinetics of this attack. It appears to confirm a functional relation between time and methane pressure, especially at higher temperature where kinetics would be expected to be limiting.

The behavior shown in [Figure 25](#) is approximately in the form:

$$\text{Rate} = A + \frac{Q}{T} + n \log P_{\text{CH}_4} \quad [30]$$

While Nelson's time dependent curves are clearly not in the correct positions for all carbon steels, the potential for correlating behavior with methane pressure is indicated. It is reiterated

here that, at low temperatures, kinetic factors prevent achieving the high methane pressures calculated even at defects or inclusions where nucleation of voids is easy

At high temperatures, equilibrium calculated pressures will not be achieved if surface connected cracks form. Thus, [Figure 25](#) and the comments here about the role of high temperature strength are presented to suggest behavioral limits and not the actual pressures achieved.

Also, there are substantial uncertainties with regard to the free energy calculations upon which the methane pressures are based. It has been reported that M_3C in alloy steels contains small percentages of Mn, Ni, and carbide formers, such as Mo or Cr, that reduce the free energy of the cementite phase, and therefore, decrease the potential methane pressure. The recent reports about attack of C- $\frac{1}{2}$ Mo steel below Nelson's curves suggests that such reductions in the free energy of Fe_3C , even associated with molybdenum, are not large. The superior tensile and creep strengths of the 0.5% Mo and Mn-Moly steels may explain the original basis for optimism about the behavior of the low molybdenum steels.

Geiger and Angeles (22) examined the equilibrium constant, K or K_{eq} ([Table 2](#)) for the methane reaction, considering the effects of alloying elements on the free energy of formation. Their results are reproduced below. The expected alloy element content in Fe_3C would only reduce K by at most 50% and would not have a drastic effect on the methane pressure, as may be judged from [Figure 10B](#). For example, comparing carbon activity of 1 and 0.5, the reduction in methane pressure is about 20%. Significant reductions in methane pressure would only be associated with the K values shown for carbides in 1Cr- $\frac{1}{2}$ Mo steel or 2 $\frac{1}{4}$ Cr-1Mo steel with higher alloy carbides such as Cr_7C_3 or $Cr_{23}C_6$.

Table 2—Values of Equilibrium Constants, K (Equation [2]), for Various Carbides

Carbide	Values of K at Different Temperature			
	900 °F	950 °F	1000 °F	1100 °F
Iron Carbides				
(1) Fe_2C , $\text{C}(\epsilon\text{-carbide})$	5.37×10^4	2.04×10^4	8.70×10^4	1.74×10^3
(2) Fe_3C	11.00	5.65	3.10	0.98
Untempered Alloy Carbides				
(3) $(0.005\text{Mo}, 0.995\text{Fe})_3\text{C}$	9.26	4.79	2.67	0.910
(4) $(0.01\text{Cr}, 0.005\text{Mo}, 0.985\text{Fe})_3\text{C}$	8.49	4.38	2.48	0.846
(5) $(0.0125\text{Cr or Mn}, 0.005\text{Mo}, 0.9825\text{Fe})_3\text{C}$	7.69	4.00	2.28	0.771
(6) $(0.0225\text{Cr}, 0.01\text{Mo}, 0.9675\text{Fe})_3\text{C}$	6.85	3.60	2.03	0.699
(7) $(0.03\text{Cr}, 0.005\text{Mo}, 0.965\text{Fe})_3\text{C}$	6.65	3.50	1.98	0.680
(8) $(0.03\text{Cr}, 0.01\text{Mo}, 0.98\text{Fe})_3\text{C}$	6.09	3.31	1.67	0.649
Tempered Alloy Carbides				
(9) $(0.04\text{Mo}, 0.96\text{Fe})_3\text{C}$ in $\frac{1}{2}\text{Mo}$ Steel	6.93	3.62	1.99	0.708
(10) $(0.04\text{Mo}, 0.96\text{Fe})_3\text{C}^*$	5.71	3.00	1.67	0.565
(11) $(0.2\text{Cr}, 0.8\text{Fe})_3\text{C}$ in $1\text{Cr}-\frac{1}{2}\text{Mo}$ Steel	2.24	1.21	0.704	0.270
(12) $(0.2\text{Cr}, 0.6\text{Fe})_3\text{C}$ in $2\frac{1}{4}\text{Cr}-1\text{Mo}$ Steel	1.81	0.980	0.589	0.230
(13) $(0.2\text{Cr}, 0.6\text{Fe})_3\text{C}$	1.29	0.751	0.456	0.152
Pure Carbides				
(14) Mo_2C in $\frac{1}{2}\text{Mo}$ Steel	1.32	1.07	0.87	1.11
(15) Mo_2C^*	5.04×10^{-4}	4.07×10^{-4}	3.39×10^{-4}	2.29×10^{-4}
(16) Cr_7C_3 in $1\text{Cr}-\frac{1}{2}\text{Mo}$ Steel	1.33×10^{-2}	1.12×10^{-2}	9.85×10^{-3}	1.16×10^{-3}
(17) Cr_7C_3 in $2\frac{1}{4}\text{Cr}-1\text{Mo}$ Steel	2.62×10^{-3}	2.20×10^{-3}	1.96×10^{-3}	2.91×10^{-3}
(18) Cr_7C_3	1.03×10^{-4}	8.90×10^{-5}	7.76×10^{-5}	5.75×10^{-5}
(19) Cr_{23}C_6 in $1\text{Cr}-\frac{1}{2}\text{Mo}$ Steel	1.01×10^{-1}	9.15×10^{-2}	8.44×10^{-2}	1.09×10^{-2}
(20) Cr_{23}C_6 in $2\frac{1}{4}\text{Cr}-1\text{Mo}$ Steel	5.25×10^{-3}	4.73×10^{-3}	4.32×10^{-3}	1.14×10^{-2}
*Carbide is assumed to be in equilibrium with ferrite whose composition is the same as the metal content of the carbide.				

Geiger's computations (22) for more complex carbides include assumptions about the ferrite content that are not always practical.

4.0 Methane Pressure Relations With Cementite

Very high methane pressures are expected in the presence of cementite, even at low hydrogen partial pressures. At 450 °F to 550 °F ([Figure 26](#) to [Figure 28](#)), at unit activity, methane

pressures on the order of the true strength of ordinary steels would be achieved at less than 100 psi hydrogen. Alloying of M_3C with small amounts of strong carbide formers like molybdenum, thereby reducing the potential carbon activity, only increases the limiting hydrogen pressure by 20% or less. In accordance with Geiger's (22) work maximum reductions in activity by a factor of 2 to 4 are considered to be reasonable for purposes of understanding the behavior of cementite.

At 600 °F ([Figure 29](#)), hydrogen pressures in line with service experience with carbon steel can be justified. As shown in the figure, 100 psi corresponds to methane pressures in the normal tensile strength range. Higher strength steels of the manganese and half-molybdenum types should be beneficial at 600 °F to 650 °F ([Figure 29](#) and [Figure 30](#)). At the lowest activities expected for C- $\frac{1}{2}$ Mo steels, hydrogen pressures above 400 psi to 500 psi would be on the margin.

For many carbon steels, creep is anticipated at 650 °F and above. For them, only 100 psi hydrogen would produce methane pressures high enough to cause creep on a local scale and, as a consequence, void growth. Enrichment of the M_3C with alloying elements would produce a stronger alloy and lower carbon activity. Still less than 200 psi hydrogen would lead to failure unless cavity nucleation and the methane reaction are slow.

At 700 °F ([Figure 31](#)), all carbon and carbon-0.5% Mo type steels containing cementite would be expected to be in their creep ranges at the stresses of interest. Methane pressures in the neighborhood of only 30 ksi might lead to failure. Hydrogen partial pressures in the range of 80 psi to 150 psi would seem to be the maximum acceptable. As a point of reference at ASME design stresses (31) in the creep range, strain rate is usually negligibly small—less than 10^{-8} /hr. An internal methane pressure numerically equal to the design stress level would not be expected to be adequate to promote expansion of a void at a rate of practical concern.

Hydrogen partial pressures similar to those at 700 °F would seem to be limiting at 750 °F ([Figure 32](#)). Creep strengths in the range of 20 ksi to 25 ksi are the practical limit for these steels. Increasing the temperature to 800 °F reduces the stress above which creep rates would be acceptable by about one third, but only slightly increases the acceptable hydrogen pressure ([Figure 33](#)).

The story is identical at 850 °F ([Figure 34](#)) where about the same hydrogen pressures correspond to the design creep strength at that temperature. At 900 °F, ASME design creep stress for carbon steel is about 6.5 ksi. A methane pressure of that value corresponds to the same hydrogen pressure shown in the above noted figures for lower temperatures, i.e. about 100 psi at the higher values of activities and at most 200 psi for M_3C with the lowest activity of carbon (i.e. with the highest percent alloy content). Finally, at 1000 °F, where the ASME design value for carbon steel is 2.5 ksi, somewhat higher hydrogen pressures might be tolerable ([Figure 36](#)).

It is remarkable that throughout the creep range, the strength reductions for these cementite containing steels are almost exactly balanced by changes in the free energy-fugacity relations to give nearly constant acceptable hydrogen pressures. There is no fundamental reason why the free energy of formation of methane and the creep strengths of steels should engage in this balancing act. It is amazing that Nelson suggested the consequences of this interaction in his predictions.

5.0 Steels With More Stable Carbides

Steels containing elements with a strong affinity for carbon (i.e. molybdenum, chromium, vanadium, titanium, etc.) are strengthened to resist creep deformation. These elements also decrease the methane pressure possible through reductions of the carbon activity and of the reaction rate. The amount of carbon left in solution correlates with activity as shown in [Figure 37](#). Thus the reduction is beneficial both kinetically and thermodynamically.

If large improvements in resistance to HTHA are to be obtained there must be sufficient alloy content to substantially eliminate all of the metastable Fe_3C or similar M_3C carbides. It is the least stable carbide in a material that governs its resistance to hydrogen attack.

The trend of the effect of carbon activity on methane pressure may be judged from [Figure 38](#). For this report, we can use rough estimates of dissolved carbon content as the activity in the more highly alloyed material, rather than complex calculations of the free energy of the carbides. Both routes should lead to the same calculated methane pressure because carbides in the steel are assumed to be in thermodynamic equilibrium with the carbon in solution. The more stable the carbide, the lower the amount of carbon left in solution and the lower the methane pressure. A note of caution is offered here. A detailed examination of the results of calculations of the free energy changes associated with complex carbides shows the corresponding methane pressures and carbon activities to be extremely sensitive to assumptions made about the resulting compositions of the adjacent solid solutions. In reality, PWHT times and temperatures and cooling rates influence the alloy content of the carbides and ferrite. The result is substantial uncertainty about the limits on the behavior to be expected.

The equilibrium equation for formation of methane shows that the fugacity of methane is proportional to the carbon activity. Lower concentrations of dissolved carbon also slow the reaction producing methane. The presence of strong carbide formers then provides three-fold benefits—strengthening, methane pressure reduction, and slower methane formation.

6.0 Behavior of Steels With Complex Alloy Carbides

Included in this group are alloys ranging from 1 $\frac{1}{4}\text{Cr}$ - $\frac{1}{2}\text{Mo}$ to higher chromium-moly-vanadium steels.

The addition of elements with strong carbide-forming tendencies reduces the activity of carbon in solution and increases tensile and creep strengths of the steel. First, we will look at the potential effects on activity and temperature. [Figure 39](#) shows the behavior for carbon activities from 0.01 to 0.15 at 450 °F. At this low temperature, it is unlikely that the methane forming reaction would proceed at a significant rate. It is also unlikely that the nucleation rate would be significant in modern, clean, higher-strength steels. Thus, almost any pressure can be tolerated.

[Figure 40](#) suggests that at 700 °F, steels with activities below about 0.06 can endure very high hydrogen pressures. Tensile strengths should not be too low and creep rates would not be of concern for steels richer in alloy content than 1 or 1- $\frac{1}{4}\text{Cr}$ - $\frac{1}{2}\text{Mo}$ steels. The expected activity levels of 0.15 or 0.10 for those materials would be satisfactory, even tempered to relatively low tensile strengths. For 1 or 1- $\frac{1}{4}\text{Cr}$ - $\frac{1}{2}\text{Mo}$ steels, it appears that pressures of the order of 1200 psi to 1500 psi might be acceptable, in line with experience with that alloy. For activities expected with 2 $\frac{1}{4}\text{Cr}$ -1Mo steel, say in the neighborhood of 0.06 or lower, acceptable hydrogen pressures would be higher, perhaps above 3000 psi. The reaction rate would be slow, given the very low concentration of free carbon and the low temperature.

At 750 °F ([Figure 41](#)), acceptable hydrogen pressures increase, but the low chromium steels would be questionable for service if carbon content is high and alloy content is insufficient to ensure freedom from M_3C type carbides. More than 1000 psi hydrogen might be acceptable for the leanest alloys. The threshold for creep may be at about the yield strength levels for these steels at 800 °F ([Figure 42](#)). Kinetics of the methane reaction might be slow given the low amount of dissolved carbon in the highly alloyed materials. However, for 1 or 1-¼Cr alloy steels (activity 0.1 to 0.15) with yield strengths at temperature in the 30 ksi to 40 ksi range and for 2 ¼Cr-1Mo steels (activity 0.03 to 0.06) with 5 ksi to 10 ksi higher yield strengths, the acceptable hydrogen pressures seen in [Figure 42](#) are in line with common applications for the respective alloys.

[Figure 43](#) to [Figure 45](#) depict potential methane pressures in the critical range of temperatures from 825 °F to 900 °F. These temperatures are of interest in predicting the behavior for high temperature hydroprocessors. Over this range of temperatures the reductions in creep strength with temperature are not exactly offset by the changes in the free energy of methane formation and the resulting reductions in methane pressure. However, the corresponding decreases in limiting hydrogen pressures with increasing temperature are small over this range.

With this picture of the importance of both strength and reaction kinetics as influenced by carbide precipitation, it may be instructive to briefly consider past research on hydrogen attack phenomena before proposing details of a technical basis for arriving at safe limit curves.

7.0 Research Studies

The API RP 941 document covers several low alloy and carbon steels produced in many product forms and for many specifications. Broadly speaking, these are carbon steel, C-½Mo steel, 1Cr- and 1 ¼Cr-½Mo steel, and 2 ¼Cr- and 3Cr-1Mo steel. However, most studies have been devoted to C-½Mo steel and 2 ¼Cr-1Mo steel. As a result, the observations herein are skewed by the behavior reported for these two very different steels.

Shortly after adoption of API RP 941, considerable research was funded by the petroleum industry. Studies by Allen (17, 21), Geiger (22), Vitovec (24), and others were creative, thoughtful, and informative. However, they were limited in their ability to interpret results because of their lack of understanding of the non-ideal gas behavior of methane and the crude Metallographic tools to study void growth available at the time. Then, starting about 25 years ago and for a period of about 10 years, there was intensive experimental and analytical work devoted to explaining HTHA. It was aimed at predicting the proper positions of the Nelson Curves. Key university investigators were Johnson (10, 32), Shewmon (32–46), Li (47–49), and Odette (8, 11). They proposed models that continue to be elaborated and refined today with advanced computational tools, but without major changes in the approaches. Extensive experimental work from Japan, focusing on C-½Mo steel, was reported in the same time frame (50–60).

Except for MPC's test programs on the effects of stress on HTHA of 2 ¼Cr-1Mo steel (61–64), experimental work was abandoned in the 1990s. Recently, parallel programs (9, 12–16, 65) in Japan, Europe, and America have addressed HTHA, but primarily from the analytical rather than the experimental side. The studies have not been entirely complementary because of the differing approaches taken. However, the international activities bring the earlier concepts up-to-date and provide some new insights (see Annex F and Annex G).

A lengthy, scientific treatise on HTHA research is avoided here because it would be inconvenient for a petroleum engineer to put into a practical context, would submerge the important points in scientific jargon, and would be repetitive of the excellent literature cited above. Interpretation and application are emphasized here at the expense of scientific and mathematical detail.

8.0 Studies

The post-Nelson studies of HTHA referenced above may be divided into several categories by date and investigator or program. These were:

- 1) Numerous API funded studies, principally by Allen, Geiger, Vitovec and their colleagues in the 1960s.
- 2) Intensive research at universities with U.S.D.O.E. support in the 1970s and early 1980s.
- 3) MPC's experimental studies of the effects of hydrogen and stress on high-strength chrome-moly steels in the 1980s and 1990s.
- 4) Studies of C-0.5Mo Steel in Japan in the 1980s and 1990s under JPVRC.
- 5) Modeling of void growth and decarburization in chrome-moly steels using FEA in Europe in the late 1990s and beyond.
- 6) API/JPI studies of C- $\frac{1}{2}$ Mo steel in Japan and America in the 1990s to date.

API took the initiative to understand HTHA after Nelson's work. Their committee-directed studies provided insight into the effects of some variables on attack rates, but at pressures and temperatures far too high to represent service. These studies included examining the effects of temperature, cold-work, and composition (17, 21). However, the tools of the day for modeling behavior were limited and the details of the attack process were inadequately understood. It is difficult to use that early data on the effects of temperature, pressure and metallurgical variables to verify new models because the degree of attack was not quantified and the materials tested were not adequately described or characterized.

Enlightening work on attack rates was performed by Steuber and Geiger (66), and later by Geiger with others (22, 67). In their work, the progress of attack in pressurized tubes was monitored by methane release rates, metallographic examinations and hydrogen flux measurements. These are the few studies in which the kinetics of attack were monitored and from which attack rates might be deduced. They exposed the interiors of carbon and low alloy steel tubes to high pressure, but relatively too high-temperature hydrogen for practical extrapolation purposes. Unfortunately, their analysis of their data may have included errors or oversights that led to some confusing or incorrect conclusions. Also, they were hampered by the shortcomings of metallurgical and thermodynamic tools of their day. Much more could be learned today with new experiments with modified test methods and analytical approach for the data. Even so, because of the importance of their observations, it is useful to consider their results in some detail here.

Steuber and Geiger observed that permeation rates through the tube walls increased with time because surface connected fissures formed by attack reduced the effective wall thickness of the tubes. Fissuring was detected when methane was released from the tube's interior wall surface. They concluded that leveling off of the hydrogen permeation rates with time after an initial period of linear increase could be related to a threshold methane pressure (fugacity) at the deepest point of attack and cessation attack at that depth. One problem is their calculation of

the methane pressure (actually fugacity) at the deepest point of observable damage may not have adequately adjusted for surface connected fissuring. They acknowledge the surface connectivity of fissuring in their discussion of peaks in methane measurements and their data appear to be accurate and consistent. However, reanalysis of their permeation data today suggests that only 40% to 45% of the total depth of attack was associated with surface connected fissures. A correction for this error would provide an estimate of the hydrogen concentration (methane pressure) at which damage for the period of exposure could no longer be observed Metallographically. Modifying and repeating their experiments today might be fruitful.

A second problem with their conclusions is the leveling off of permeation and the apparent reduction in the rate of attack reported by Steuber and Geiger was due to a limitation of the rate of hydrogen absorption into the tube wall, not an attack threshold. The uncracked wall thickness of their tube wall decreased with time. When the wall is too thin, the hydrogen content in the metal cannot reach Sievert's solubility limit unless the rate of adsorption at the solid/gas interface can increase in proportion to the reciprocal of the remaining ligament. The maximum concentration of hydrogen during Steuber's and Geiger's (single-side) exposure of pressurized tubular specimens was probably limited by the absorption rate of hydrogen from the pressurized tube interiors. In some cases the wall thickness was reduced only a small amount before attack leveled off, but because of the high hydrogen diffusivity at the very high temperatures they used, it is possible that the flux (absorption rate) limited attack in their thin wall experiments.

When adsorption limits the flux, the concentration of hydrogen in the metal may be far from the equilibrium value. Since methane fugacity varies with the square of the effective hydrogen pressure and the hydrogen pressure varies with the square of concentration, small reductions in surface hydrogen content have large (fourth power) effects on the actual methane pressures that would be achieved.

The methane fugacity-pressure (non-ideal gas) relationship and access to computing capability enabled Odette (19, 20), Johnson (10), Li (48) and others to seriously attempt to model behavior. These researchers used essentially the same creep/diffusion void growth models, thermodynamic relations and non-ideal gas equations described earlier. However, their work was limited by lack of knowledge of key materials properties and behavioral data. These deficiencies included data on materials strength, carbon activity, surface and grain boundary diffusivities, bubble growth kinetics and the effects of temperature and impurities on each of the above.

These researchers assumed "Nelson Curves" to be correct for the purpose of checking their models (as is done herein). However, in most cases the curves appeared to be too conservative in light of experience and there was no validation by long-term tests. Therefore, the curves lacked credibility and were never accepted. Reports of successful experience with chrome-moly steels, beyond the limits suggested by the researchers, led to the conclusion that the models might be missing something. Interest in using those analytically derived results eventually declined.

JPVRC studies (51, 57, 58, 68–71) of C-½Mo steel revealed significant differences between two heats that were extensively studied. As expected, there were beneficial effects of tempering and adverse effects of very high temperature weld thermal cycles on susceptibility. It was concluded that Shewmon's P_v and P_w (Annex F) equations for the attack rate might be used to describe time-pressure-temperature relations of the general shape of Nelson Curves for C-½Mo steel. The coefficients in the P_v and P_w curves for one steel studied were adjusted to be close to the final C-½Mo line in the then current edition of API RP 941. This basic P_v or P_w curves can be

shifted up or down in P-T space by adjusting one or more coefficients to intersect limited data for any material.

Hattori (73, 74) modified the P_w concept by including a factor for “bad” $M_{23}C_6$ carbides in the 0.5 5 Mo steel. However, others have not corroborated his conclusions about $M_{23}C_6$ or concurred about its existence in commercially supplied, normalized and tempered heats of C-½Mo steel. Details of the carbide Hattori reported went unconfirmed by others and the HAT or Hydrogen Attack Tendency Chart proposed by Hattori is not in widespread use. However, his work did put the spotlight on the detrimental effects of coarse carbides. All agree that coarse carbides may serve as plentiful nucleation sites and should be viewed negatively.

Other JPVRC studies in Japan consisted mainly of exposures to very high pressure hydrogen for short times followed by measurement of tensile or impact properties. That work did not include modeling and did not incorporate predictions based on materials' properties, thermodynamics, or reaction rate measurements to clarify or quantify details of behavior. However, the experiments by JPVRC did contribute to the growing body of evidence that the early C-½Mo steel lines had been incorrectly (optimistically) placed. High impurity content was concluded to be an indicator of increased susceptibility to hydrogen attack. The material found to be inferior in those studies had higher impurity (S, P, etc.) content. (It also had high aluminum content.) Unfavorable experience in the field with heats containing high levels of tramp elements seems to validate the conclusions of JPVRC.

Shewmon's P_v and P_w concepts were reexamined in the JPVRC study and during the work of the Japanese team in API's activity, as described in Annex F. The discussion in Annex F uses the C-½Mo lines in API RP 941 as the template for projecting behavior to other alloys. Acknowledging the importance of methane pressure the investigators rationalized the curve shape without getting into rigorous detail about the attack process. They modified Shewmon's P_w equation for the initial attack (expansion) rate to predict failure time and quantified the expected trends based on temperature, hydrogen pressure and fugacity of methane. A comparison of P_v and P_w is worthwhile at this point. They are not equivalent or interchangeable. Setting t equal to life:

$$P_v = \log P + 3.09 \times 10^{-4} T (\log t + 14) \quad [31]$$

or

$$\log t = -14 + P_v - \log P / (3.09 \times 10^{-4} T) \quad [32]$$

while

$$P_w = \log t + 3 \log P - \frac{9918}{T} \quad [33]$$

or

$$\log t = P_w - 3 \log P + \frac{9918}{T} \quad [34]$$

In the P_v case,

$$\frac{\partial \log t}{\partial \log P} = \frac{-1}{(3.09 \times 10^4 T)} \approx -(4 \text{ to } 5) \quad [35]$$

while in the P_w case,

$$\frac{\partial \log t}{\partial \log P} = -3 \quad [36]$$

P_v predicts a much stronger dependence on hydrogen pressure (hence hydrogen concentration) than does P_w . This is a big difference. At temperatures of interest, for C-½Mo steel at 700 °F, the pressure dependence of P_v is fifth order, a surprisingly high number in light of models and observations of gradients in through wall damage. Actually, neither P_v or P_w does well predicting observed damage gradients. The through-wall damage gradients implied by P_w and by P_v at usual operating temperatures for C-½Mo are shown in [Figure 47](#).

The gradients depicted in [Figure 47](#) would be expected prior to the appearance surface connected cracking or blistering. It is assumed Sievert's and Fick's Laws apply, i.e. the effective hydrogen pressure varies with the square of the concentration of hydrogen at any point in the metal and flux is proportional to the (linear) concentration gradient. Additionally, it is presupposed that the delivery (diffusion) of carbon and hydrogen to sites (voids) for the reaction to form methane does not limit the rate of attack. The result is that damage is predicted to decrease with the through-wall distance more rapidly than has typically been observed.

Examination of the attack gradients in components exposed to hydrogen on one side suggests that gradients shown in [Figure 47](#) are much too steep. For comparison, a profile shown in the [Figure 47](#) uses methane pressure as a driving force. It suggests a flatter curve and deeper penetration of visual damage. Attack is often seen more than halfway through the wall in one-sided exposures. Such observed behavior cannot be reconciled with expressions of the P_v and P_w form. Also, calculations for P_v and P_w do not take into explicit account for acceleration of the attack with the passage of time due to the simplifications introduced to make the model more practical for implementation. Annex G provides insight into the complexity required to fully model all the factors contributing to the time dependence of damage.

9.0 Effect of Stress

Few studies of the effects of stress on hydrogen attack have been reported. The most comprehensive program was that of MPC. MPC studies of the effects of stress have been reported in detail elsewhere (64). They showed that for stress rupture specimens tested in hydrogen under moderate applied stresses, HTHA was accelerated and occurred below Nelson's lines. The materials studied were base metal and welded 2 ¼Cr-1Mo and 3Cr-1Mo steel tempered to typical as well as relatively high strength levels. Some observations previously reported are updated here. The first MPC studies involved base metal which showed attack, in long-term exposures. Then, the work explored the behavior of weldments.

The heats studied were representative of modern low impurity materials. The weldment from which specimens were made was a typical submerged arc joint between two heavy plates from different producers. The two heats of 2 ¼Cr-1Mo utilized will be referred to herein as the 12-in. (30-cm) and the 13-in. (32.5-cm) heats.

While carbon activity was not measured directly, there was an expectation that for the heat treatments studied reduced carbon activity should be associated with increased tempering temperature (or Larson-Miller parameter). Values of 0.03 and 0.06 are used elsewhere in this report for carbon activities resulting from high (1275 °F) and low (1165 °F) temperature tempering, respectively. These are estimates and are consistent with measurements made by Shewmon and referenced in another MPC study, (75, 76).

For the tests in hydrogen, welded samples were heat treated in two ways. One heat treatment provided an accumulated temper parameter of 36.79 equal to 16 hours at 1275 °F. The other parameter value was 34.74 for 24 hours at 1165 °F. These heat treatments corresponded to tensile strengths of approximately 85 and 102 ksi, respectively, and cover the strength range found for accelerated cooled materials placed in service over the last thirty years. A large database compiled from creep-rupture tests of these same materials and weldments in air was used for comparative purposes.

The effect of stress may be seen directly from several tests of the 12-in. weldment shown in [Figure 48](#). For material given the 1275 °F temper, three tests at 850 °F show a relatively small increase in life (a factor of 2) with decreasing stress between 37 and 28 ksi. In air, an increase in life by a factor of 10 would be expected. Further reduction of stress to 25 ksi suggests a flattening of the slope, but the relative life fraction as compared to tests in air was not improved. At 825 °F, the slope of the rupture line was about the same as in air, but lives were only about one-third as long. At 900 °F, the effect of hydrogen was greater and the curve steeper than in air. The locations of the failures were in the heat affected zones of the weldments and not in the base metal or filler metals.

For the same material tempered at 1165 °F, tests at 3000 psi hydrogen and 900 °F showed only a small effect of stress at 28 ksi and 25 ksi ([Figure 48](#)), but a greater increase in life with further stress reduction.

This data suggests a complex interaction between hydrogen pressure and stress as described later.

10.0 Effect of Temperature

As shown in [Figure 49](#), for the 12-in. plate tempered at 1275 °F, there was only a factor of 2 increase in life when the test temperature was reduced from 850 °F to 825 °F at 37 ksi. A larger increase in life at 33 ksi was observed. This may be only scatter in data considering the life at 30 ksi was shorter. The Larson-Miller parameter for behavior in air leads to the expectation of a factor of about 3 for a 25 °F change in temperature. At 28 ksi, decreasing temperature from 900 °F to 850 °F resulted in an increase in life by only a factor of 3, i.e., again less than a factor of 2 per 25 °F instead of 3. However, at 25 ksi, the ratio was somewhat greater.

Clearly, under hydrogen, the effect of temperature is dependent upon stress and may be complex in the vicinity of the Nelson Curve limits. This is to be expected since decreasing temperature increases the potential methane pressure relative to the applied stress and should shorten life. While creep rates are slowed, details of the interaction of applied stresses and internal methane pressures are a matter for speculation at this point.

11.0 Effect of Hydrogen Pressure

The effect of hydrogen pressure was observed to be remarkably consistent and apparently independent of material. The trend may be seen in [Figure 50](#). All data shown are for material tempered at 1165 °F. Starting with the tests on 12-in. plate at 850 °F and 33 ksi, life increased by a factor of 2 from 10,387 hours to 22,363 hours as hydrogen pressure decreased from 3000 psi to 2000 psi.

At 900 °F and 28 ksi, the relative effect was precisely the same, life increased from 3,697 hours to 7,490 hours with the reduction in pressure. For the tests of the weldment involving the 13-in. plate, the life observed increased from 15,327 hours to 31,450 hours. However, the failure location changed from fine grain to coarse grain heat affected zones. Of course, there was also extensive hydrogen attack damage in the fine grain region at failure.

It was to be expected that rupture life would be an inverse function of pressure. The data collected suggest an exponent of about 2, i.e., life varies with the reciprocal of pressure squared. Shewmon (35) projected approximately that figure for quenched and tempered material. He stated that strain rate due to bubble formation should be proportional to hydrogen pressure to the 2.2 power.

11.1 Materials Issues

Tests in air had revealed that the 12-in. material, welded or not, always exhibited superior behavior as compared to the 13-in. material. The behavior of the two weldments in hydrogen can be compared at each of five identical test conditions studied ([Figure 51](#)). For materials heat treated at 1275 °F, the tests at 850 °F, 3 ksi hydrogen pressure and 33 ksi stress yielded 5,782 hours for the 12-in. weldment and 22,192 hours for the 13-in., a difference of a factor of 4. For the heat treatment at 1165 °F, tests were conducted at 850 °F and 900 °F at hydrogen pressures of 3 ksi and 2 ksi. At the higher pressure, a factor of 4 was observed again. The lives of the 12-in. and the 13-in. materials were 3,697 hours and 15,327 hours, respectively. At the lower pressure and 900 °F, the respective lives were 7,490 hours and 31,450 hours, also a factor of 4 (see [Figure 51](#)). The life ratios of the different materials in hydrogen were then quite similar to those observed in air. Superior creep strength was retained under hydrogen. This suggests a direct correlation in the creep range between resistance to HTHA and creep strength.

12.0 Exposure Time or Stress

The results reported above quantify the effects of important variables on the hydrogen attack susceptibility of 2 ¼Cr-1Mo steel. While the trends are not surprising, the data developed were used to correlate behavior for the purposes of assessing the interaction of hydrogen pressure and stress, as described later. It was found that longer term (lower stress) tests tended to show increasing amounts of degradation at given hydrogen pressures, as shown in [Figure 52](#). However, it was recognized that the trend was complex and not easily quantified at the time.

It was concluded from the MPC study that optimizing resistance to hydrogen attack requires PWHT at relatively high temperatures (1275 °F). Hydrogen attack susceptibility appeared to be greatest in the Heat Affected Zone and varied from heat to heat due to inherent differences in creep resistance (consistent with cavity growth models). The data indicated that for operating conditions of 825 °F and above, hydrogen attack might be anticipated in highly stressed components of 2 ¼Cr-1Mo, given minimal PWHT. When higher operating temperatures are anticipated, a vanadium modified alloy is appropriate. Creep strength and resistance to hydrogen attack for vanadium modified heats developed and studied under MPC (64) were far

superior to conventional 3-Chrome grades which do not contain vanadium, but which have been used in the past at higher temperatures than 2 ¼Cr-1Mo steel, but only at low stresses.

API has assigned the 2 ¼Cr-1Mo-V alloy, developed under MPC's project, the same position on the Nelson Curve as the 3-chrome grades. MPC exposed the base metal of its vanadium bearing grade for about 100,000 hours under high stress in 3000 psi hydrogen at 950 °F without failure. The carbon activity estimate for base metal of this grade is 0.01 and is generally consistent with the estimates made using methods reported in Annex G by European investigators. For the HAZ of a weldment, higher values of the carbon activity would be appropriate.

13.0 European Studies

Recent European work greatly advanced modeling of attack-related phenomena. Abstracts and commentaries are attached in Annex G. Researchers at Delft University (12–16) explored non-uniform cavitation processes on the grain size scale in polycrystalline aggregates. Analyses were made of the influence of the surrounding grains on development of grain boundary attack. Numerical results were explained in terms of two simplified models for the grain deformation-grain boundary cavitation interaction process.

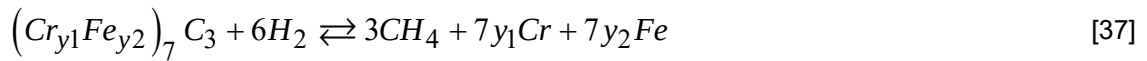
Building on their earlier work, the Delft investigators extended a cavity growth model in which diffusion and creep were coupled. They performed detailed numerical analyses of the possible stress states that may be encountered. The combined effect of internal methane and hydrogen pressures and applied stresses were computed. The technique was applied to predict failure in 2 ¼Cr-1Mo steels based on estimates of the free energies of the carbides present.

The Delft work first indicated how attack develops in time. It was assumed that the cavities were distributed uniformly along the grain boundary facets. For the later work they noted carbides are not uniformly distributed over a grain facet and, more importantly, the carbides can have different compositions leading to significant differences in the methane pressure that may form. They noted too that, grain boundary cavitation would be slowed by surrounding grains, which deform by creep, only very slowly. Thus, the results of computer simulations of cavitation in a polycrystalline aggregates differed from those obtained for simple single cavity models.

A two-dimensional polycrystal model of Van der Giessen and Tvergaard (15) was used to study the influence of carbide variations under different conditions. They showed that the growth rate of cavities in a creeping matrix is very strongly dependent on stress triaxiality. They concluded that void growth models may predict growth rates that are several orders of magnitude in error, depending on stress triaxiality and porosity.

Application of the Delft model to 2 ¼Cr-1Mo (13) steel indicated that the time to failure is very sensitive to the type and composition of the carbides in the material since these determine the equilibrium methane pressure. The investigators at Delft predicted the same for other materials. They also concluded that there would be strong sensitivity to heat treatment, consistent with the observations reported above for MPC's experiments. The Delft researchers' model confirmed the importance of stress. Stresses could be either residual or due to the applied loading. The effect of stress was related primarily to the methane pressure through a triaxiality parameter and a pseudo length parameter. In short, the Delft researchers concluded that there are two cavitation modes that can be covered by continuum damage relations. In one case, the grains can deform significantly, the cavitation concentrates primarily on facets perpendicular to the macroscopic maximum principal stress. In the other, creep deformation of the grain is negligible and cavitation develops uniformly on all facets.

Recently, Schlogl and Van der Geissen synthesized their results of modeling and finite element analysis into a coherent picture of the progress of hydrogen attack in a welded 2 ¼Cr-1Mo steel pressure vessel (77). Their story is valuable because, through attention to details, it addresses all the issues that may arise in any steel and component. They note the presence of multiple carbides—in this case M_7C_3 , M_6C , and M_2C . Since in low alloy steels, the carbides are not pure (i.e., binary, a metal and carbon), the thermodynamic driving force for methane formation is not known with precision. There is then significant uncertainty in the methane pressure calculation. Their approach is traditional; they write the equilibrium equation for the chemical reactions describing the breakdown of the carbides by hydrogen to form methane, e.g.:



For alloy steel with lower percentages of carbide forming elements than 2 ¼Cr-1Mo, the potential existence of M_3C , essentially Fe_3C , is of paramount concern, and one need not usually proceed much further if its presence is expected. The reason is that where cementite type carbides are found the free energy driving force for methane formation, and likely the thermodynamics of behavior will be dominated by that phase. While M_3C type carbides may include molybdenum, chromium, manganese, or other elements, carbides of the $M_{23}C_6$, M_2C , or M_6C types are far more stable and are not expected to influence behavior.

The process used by Schlogl, et al (77), is to estimate the Gibbs free energy by writing an equation for the equilibrium state of the above reaction as follows:

$$3\mu_{CH_4} + 7y_1\mu_{Cr} + 7y_2\mu_{Fe} - 6\mu_{H_2} - \mu_{M_7C_3} = 0 \quad [38]$$

For the carbide M_7C_3 which they anticipate will be the “main” carbide of importance (one should always seek the least stable carbide present on the assumption that it will be most easily reacted and generate the highest methane pressure), the following form is used:

$$\mu_{M_7C_3} = G_m^{M_7C_3} = y_1 {}^0G_{Cr;C} + y_2 {}^0G_{Fe;C} + 7RT(y_1 \ln y_1 - y_2 \ln y_2) + y_1 y_2 L_{Cr,Fe;C} \quad [39]$$

where:

y_1 and y_2 are the respective fractions of chromium and iron in the carbide.

One may rigorously proceed to develop the free energy of the ferrite:

$$\begin{aligned} G_m^\alpha = & y_{Cr}y_{Va} {}^0G_{Cr;Va} + y_{Cr}y_C {}^0G_{Cr;C} + y_{Mo}y_{Va} {}^0G_{Mo;Va} + y_{Mo}y_C {}^0G_{Mo;C} + y_{Fe}y_{Va} {}^0G_{Fe;Va} + \\ & y_{Fe}y_C {}^0G_{Fe;C} + RT[y_{Cr} \ln y_{Cr} + y_{Mo} \ln y_{Mo} + y_{Fe} \ln y_{Fe} + 3(y_C \ln y_C + y_{Va} \ln y_{Va})] + \\ & y_{Fe}y_{Cr}(y_C L_{Fe,Cr;C} + y_{Va} L_{Fe,Cr;Va}) + y_{Fe}y_{Mo}(y_C L_{Fe,Mo;C} + y_{Va} L_{Fe,Mo;Va}) + \\ & y_C y_{Va}(y_{Fe} L_{Fe;C,Va} + y_{Cr} L_{Cr;C,Va} + y_{Mo} L_{Mo;C,Va}) + G_{mag}. \end{aligned} \quad [40]$$

and the potentials through partial derivatives:

$$\mu_{Fe} = G_{Fe} = \left(\frac{\partial G}{\partial n_{Fe}} \right)_{T,p,n_{Cr},n_{Mo},n_C} = G_{Fe;Va} = \left(\frac{\partial G}{\partial n_{Fe;Va}} \right)_{T,p,n_{Fe;C},n_{Cr;C},n_{Cr;Va},n_{Mo;C},n_{Mo;Va}} \quad [41]$$

and

$$\mu_{Cr} = G_{Cr} = \left(\frac{\partial G}{\partial n_{Cr}} \right)_{T, p, n_{Fe}, n_{Mo}, n_C} = G_{Cr; Va} = \left(\frac{\partial G}{\partial n_{Cr; Va}} \right)_{T, p, n_{Cr; C}, n_{Fe; C}, n_{Fe; Va}, n_{Mo; C}, n_{Mo; Va}} \quad [42]$$

However, Schlogl, et al., note that this is a blind alley. One must just estimate the free energies based on measurements (or guesses) of the carbide compositions and the equation for potentials above. Inserting the Gibbs free energies from all these estimates and the local hydrogen concentration (equivalent pressure) yields an estimate of the highest methane potential, its fugacity. Because methane is non-ideal and fugacity is very high, especially at the lower temperatures of interest, one uses the relation noted earlier (Equation [14]) to calculate the methane pressure of interest.

$$f_{CH_4} = p_{CH_4} e^{C(T)p_{CH_4}} \quad [43]$$

The study includes the usual concepts of damage due to coupled diffusional and creep void growth, i.e.

$$\dot{V}^{cav} = \dot{V}_{diff}^{cav}(a, b, p_m, \sigma_n, \sigma_e) + \dot{V}_{cr}^{cav}(a, b, p_m, \sigma_m, \sigma_e) \quad [44]$$

and the creep rate

$$\dot{\epsilon}_e^C = B(T)\sigma_e^n \quad [45]$$

A stress and temperature dependent “length” parameter is established, as noted earlier in Equation [24].

$$L = \left(D\sigma_e / \dot{\epsilon}_e^C \right)^{1/3} \quad [46]$$

This damage model was applied to weld metal, coarse-grain HAZ, fine-grain HAZ and base metal. Each zone had different strengths, grain size, carbides, carbon activity and potential methane pressure. Propagation of damage was studied through the hydrogen content gradient through the wall (although an error was apparently made here in taking an essentially linear effective pressure gradient through the wall rather than using the linear gradient of hydrogen concentration). Methane pressure in equilibrium with the M_7C_3 of varying chromium content was estimated.

Computations of damage gradients through the wall were examined at various life fractions as a function of the three principal stress directions. In their example, damage accumulated most rapidly in HAZ's where creep strength was the lowest.

Activities in Europe were spurred by an interest in predicting the behavior of advanced alloys under the most severe operating conditions envisioned for low alloy steels. The diffusion/creep interaction modeling carried the concepts of early void growth modelers, such as Johnson, Shewmon, and Odette, to new levels of refinement. They provide a complete, integrated approach to the effects of carbide composition, applied stress, temperature, and non-ideal gas behavior on time to failure. Limitations of the models are materials properties estimates,

confirmation of estimates of carbon activity and the absence of a database that could support the conclusions. It was concluded that carbon activity in vanadium modified low alloy steels is so low that potential methane pressures would be easily tolerated.

14.0 New Analysis of MPC Work

The results of MPC's extensive studies of 2 ¼Cr-1Mo steel were examined using the concept of methane pressure as the driving force to develop isochronous failure contours. For this work, a macrophenomenological model was used based on the following concepts:

- 1) The activity of carbon was estimated for the conditions of PWHT evaluated by MPC. The values chosen were 0.03 and 0.06 for the heavy (1275 °F) and light (1165 °F) tempering of weldments, respectively.
- 2) The line for 2 ¼Cr-1Mo steel currently in API RP 941 was assumed to be close to correct for at least 100,000 hours, unstressed service for the heavy tempering heat treatment. The corresponding methane pressures can be set equal to the design allowable stress for that temperature.
- 3) Methane pressure and applied stress were assumed to interact in producing grain boundary damage.
- 4) It was assumed that hydrogen alone could lead to failure through methane pressure development. The exponent for methane pressure dependence of unstressed failure time was estimated to be between about 4, an intermediate value between theories and rupture tests in air, absent a database failure behavior for of unstressed exposures in hydrogen.
- 5) Equations for stress-rupture lives observed in air were used. Typically, the exponent for stress-rupture behavior in air is between 6 and 10.
- 6) The relation that captures an interaction between damage in air and in hydrogen under stress was expressed as follows:

$$\frac{1}{t_{H,S}^m} = \frac{1}{t_H^m} + \frac{1}{t_S^m} \quad [47]$$

where:

m = an exponent obtained by fitting the interaction of creep and methane pressure damage modes,

$t_{H,S}$ = failure time under stress and hydrogen (methane), and

t_H, t_S = failure times in hydrogen (methane) or under stress in air, individually.

- 7) For any heat treatment of the steel, carbon activity was assigned. For the hydrogen pressure the corresponding methane pressure can be calculated.
- 8) Using the interaction exponent as a dummy variable; isochronous life predictions can be compared to available test data from MPC, European or other test programs.

For a selected time to failure, a range of applied stresses was examined. For each stress, the failure time in air was calculated. Since the equations are all in closed form, the corresponding methane and hydrogen pressures to give the target life could be calculated.

The results applying the approach above are shown for some long term MPC results (64) and the short term, high temperature tests of the European researchers (78) are plotted in [Figure 53](#) to [Figure 56](#). Applied stress is found to reduce the life in hydrogen in a complex fashion and to a degree dependent on creep strength in air. This is consistent with experience.

The best fit interaction exponents for the data, m , were found by trial, usually about in the range of $1/3$ to $1/2$. The approach was also applied successfully to very old results from work by Vitovec on C- $1/2$ Mo steel. See [Figure 57](#) (24).

The result of this exercise (curves in [Figure 53](#) to [Figure 57](#)) suggests this is a reasonable approach to modeling performance, given properties in air and some benchmarks for hydrogen performance. The pressure-applied stress contours trace the complex response to stress observed in MPC's program as described above. These pressure/stress contours suggest a starting point for developing life assessment tools and, at least in preliminary fashion, evaluating the effects of operation under variable conditions (over-heating excursions) as discussed in Annex C and Annex H.

15.0 Development of P/T Limits Near the Creep Range and Above

From the above, in the creep range at moderate applied stresses, long term hydrogen P/T limits may be estimated by finding for any temperature the hydrogen pressure corresponding to methane pressures on the order of the design allowable stress, i.e., a stress giving negligible creep. This would be consistent with void growth models. (Below the creep range, the limit may be set by the reaction rate estimating hydrogen solubility and carbon concentration in the matrix.) Examples are illustrated in the following:

[Figure 58](#) focuses on the pressure relations at temperatures of interest in the creep range for carbon steel. The hydrogen pressures corresponding to the allowable stress limits at each temperature are cross plotted. The relatively constant pressure behavior described earlier and found on Nelson's curves may be seen to lie in the neighborhood of 100 psi.

[Figure 59](#) shows the benefits of increased strength and reduced carbon activity that might be expected for a C- $1/2$ Mo or similar steel. The limiting hydrogen pressure increases because of the increased strength and lower activity expected.

Pressure limits for 1 $1/4$ Cr- $1/2$ Mo steel at carbon activity of 0.1 are found in [Figure 60](#). Pressure increases with decreasing temperature below the creep range.

Two curves are shown for 2 $1/4$ Cr-1Mo steel in [Figure 61](#) and [Figure 62](#). The first is for the heavily tempered (1275 °F, multiple cycles) variety. At typical operating temperatures, hydrogen pressures required for a clad, thick wall reactor seem consistent with the calculations. Increasing temperatures do not significantly reduce the calculated acceptable value.

Material tempered at lower temperatures (1165 °F) would be expected to have higher carbon activity and more free carbon in solution ([Figure 62](#)) and thus reduced acceptable hydrogen partial pressures. However, the acceptable hydrogen partial pressures are only slightly reduced

because these steels have enhanced creep strength. On the other hand, as a practical matter, the methane forming reaction rate at lower temperatures might be more rapid due to the increased amount of carbon remaining in solution.

Vanadium bearing steels ([Figure 63](#)) would appear to have a significant hydrogen pressure margin for current designs based on an alloy with an estimated carbon activity of 0.01.

16.0 A Technical Basis

Inspection of the plots of methane pressure and temperatures for steels discussed above suggests the reasonableness of Nelson's placements. Depending on the activities selected, the pressure limits may vary somewhat, but are within narrow ranges consistent with experience. Relating position to strength was an idea of early investigators. However, they could not quantify the non-ideal behavior of methane pressure, nor did they adequately consider materials properties including carbon activities and availability in the matrix. The plots below incorporate the concepts described above including the estimates for the effects of temperature and pressure on reaction rates. [Figure 64](#) to [Figure 67](#) provide "predictions" of where the P/T should be for carbon steel, carbon- $\frac{1}{2}$ Mo, 1 $\frac{1}{4}$ Cr alloy and 2 $\frac{1}{4}$ Cr alloy for reasonable combinations of the respective activities and creep strengths.

As noted earlier, the creep strength basis at high temperatures breaks down where a different approach is needed where reaction rates are slow.

Annex C provides guidance about strengths that may be used to develop the limits or design allowable stresses may be used. The carbon activities sufficient to explain the behavior historically observed are as follows:

Table 3—Carbon Activity

Steel	Carbon Activity	Assumption
Carbon	1	Fe_3C
C- $\frac{1}{2}$ Mo	0.5 to 0.8	M_3C
1Cr or 1 $\frac{1}{4}$ Cr- $\frac{1}{2}$ Mo	0.05 to 0.15	dissolved C
2 $\frac{1}{4}$ Cr-1Mo	0.03 to 0.10	dissolved C
3Cr-1Mo	0.03 to 0.10	dissolved C
V modified or high Cr	0.005 to 0.015	dissolved C

It has been assumed that carbon activity is related to carbon content through a multiplier in the range of unity justified in [Figure 37](#). Carbon activity depends on composition and heat treatment. This is true of strength as well. Thus, individual heats of the alloys will exhibit a range of performance, depending on composition and heat treatment.

The notion being advanced here is that if the methane pressure generated is insufficient to cause an appreciable creep rate or deformation at the microscopic level, attack will not occur. This is generally consistent with all models for void growth and avoids concern for the details of diffusion processes (Annex F and Annex G.) Analytical models over the years incorporated creep rate in the calculation, but models have suffered from poor characterization of materials'

strength parameters. They also tended to predict attack at too low temperatures, perhaps because nucleation and reaction rates are not adequately characterized with regard to carbon concentration and microstructure.

A simple solution to the problem of overestimating the tendency for hydrogen attack at low temperatures offered here is to examine the product of hydrogen and carbon contents. This concept was tested by assuming that Nelson's carbon steel line is roughly in the correct location. Hydrogen content on the attack line can be calculated and the critical product (see Equation [48]) of hydrogen and carbon estimated. The fact that it is nearly constant along the "safe lines" reinforces the argument. The inferred reaction rates were applied to the other alloys. Low alloy steels will have higher temperature plateaus, i.e. higher hydrogen pressures at higher temperatures because the amount of dissolved carbon available to participate in the reactions is lower, see [Figure C-1](#). Nucleation rates are not so easily estimated and must be viewed as dependent on microstructure (coarse carbides and inclusions being detrimental).

In essence, at low temperatures, the reaction rate is adequate to sustain attack when:

$$\text{Rate} = K = [C] [H]^m \quad [48]$$

where:

- $[C]$ = dissolved carbon,
- $[H]$ = dissolved hydrogen, and
- m = an exponent between 1 and 4.

This approach leaves open the issue of exactly where the reaction occurs, i.e. on the carbide surface or at any other interface.

17.0 Discussion

The topic of HTHA has been researched for over seventy years. The seemingly simple curves developed by G.A. Nelson (Annex A) attempted to capture industry experience through the 1950s and 1960s. With the notable exception of C- $\frac{1}{2}$ Mo steel, "the Nelson Curves" depicting satisfactory and unsatisfactory pressure-temperature regions have survived as reasonable to this day. The pressure-temperature curves he prepared were based on Nelson's judgment after considering reports about laboratory tests and plant experience. His judgment seems to have been quite good because much of the raw "data" he obtained might not stand up to close scrutiny. The information he was given by plant operators about service pressure and temperature, or the absence of damage should not be accepted at face value. This statement is made here because, even currently, we find it difficult to obtain accurate operating data and material damage assessments. This barrier to gathering reliable data is unlikely to have gotten worse since Nelson's time. While the data gathered by Nelson from the field were certainly suspect, laboratory work from his time on has not yielded conclusive information helpful in today's climate of interest in fitness-for-service, risk and life assessment.

One can debate whether Nelson's success has been the result of remarkable insight, his conservatism or just that his curves have not been effectively tested in service because of large operating safety margins used in refineries. Certainly the success of API RP 941 stems in part from the fact the curves have been conservatively applied in regard to design and operation. Recently, however, a growing list of problems with C- $\frac{1}{2}$ Mo steel underscored the lack of understanding of HTHA and heightened concern about lengthening exposure time and the

curves for other steels. Also, now it is desired to push equipment to the limits of API RP 941 for economic reasons and to perform risk-based inspection. Annex A provides a detailed discussion of the background of API RP 941 and the data gathered.

It is worth pondering why seemingly little progress in understanding HTHA has been made since Nelson's times. We are still far from being able to make quantitative predictions about the behavior of steels subject to HTHA. A literature review done for this study has led to a long list of obstacles to establishing more appropriate operating limits for steels. The list in Annex E should provide someone generally familiar with HTHA with additional insight into the nature of HTHA and the current state of affairs. Also refer to Annex A and the references cited in API RP 941 to obtain additional technical foundation.

The list in Annex E explains why there is currently inadequate data about the specific effects of microstructure, carbon activity and hydrogen content. The inconvenient aspects of studying reaction kinetics and calculating methane pressure leaves engineers poorly equipped to consider the actual driving force for initiation and propagation of attack.

This report has attempted to overcome shortcomings of prior investigations by focusing on quantifying the role of methane pressure on causing HTHA damage.

To validate a model for HTHA it would be necessary to fashion a comprehensive test program and then determine for one steel the functional relations of all key variables in hydrogen attack. Such variables are stress, grain size, tensile and creep strengths, carbon content, temperature, methane pressure, microstructure, etc. Only MPC's stress rupture results for 2-1/4Cr-1Mo in high-pressure hydrogen approach being such a database, but they fall short. The set of isochronous lines for carbon steel in API RP 941 are not a satisfactory starting point.

Finally, as noted in Annex A, Nelson reportedly created his curves by applying a safety margin of 30 °F to 50 °F to his curves for reported damage. Also, Nelson referred to depicting average material behavior. Exactly what the lines were meant to signify is unclear, but they seem to be appropriate, with one notable exception, for exposures absent high applied stresses. Today some suggest the correct C-1/2Mo curve should be only 50 °F above Nelson's carbon steel line. In other words, if Nelson applied a 50 °F safety margin for carbon steel, the newly suggested C-1/2Mo steel curve would sit essentially on Nelson's unfactored C steel curve. Despite their possible shortcomings, Nelson's lines are still a good guide to trends and are a useful basis for qualitative judgments.

18.0 Final Comment

The concept of a simple boundary between safe and unsafe operating conditions in hydrogen for common alloys, of the type depicted by the Nelson Curves should not be expected. Certainly material composition, heat treatment and stress are well accepted as variables that influence behavior. Operating above the current lines can lead to short life and time dependent failure.

Experience shows damage accumulation is time dependent. However, the methods of detection and quantification of damage are so inadequate, operating conditions so poorly recorded, failure analyses so cursory and materials characterization so primitive, that life prediction is on shaky grounds today. Studies that can now be defined utilizing knowledge of methane pressure to get at the kinetics are needed. These would permit developing correlations useful for design and for fitness-for-service.

Hydrogen content, potential methane pressure, and relative reaction rate based on standard kinetics will be needed to accurately predict behavior. A procedure for evaluation of recommended equipment would be as follows:

- 1) Using appropriate diffusivities, solubilities and fluxes, calculate local through wall effective hydrogen pressures.
- 2) Using methane pressure vs. hydrogen pressure reference lines for each alloy/heat treatment and the corresponding appropriate activity of carbon, estimate the potential methane pressure at the operating temperature.
- 3) Using the approach presented here, determine if conditions are in a range that may be potentially damaging.
- 4) Using the methods suggested herein, estimate the applied stress interaction and the damage rate.
- 5) See Annex C where operating conditions may be in the reaction rate limited regime.

NOTE It is not known if a linear life fraction rule can be justified for this application. However, for small excursions, if conservatively applied, the technique could be used.

The insights gained in preparing this Technical Basis Document suggest the outlines of studies that might profitably be conducted to test the concepts advanced herein and provide important information for Fitness for Service evaluation, inspection planning and risk based equipment management.

To begin with, the industry would benefit by developing means of quantifying the progress of hydrogen attack damage. This would facilitate communication, data gathering, documentation, reporting information to API, damage modeling and eventually predictive tools. This goal would be more readily accomplished in the context of a test program that included interrupted testing of specimens exposed to hydrogen on only one side. There is little reliable information on the time dependence of damage. Monitoring damage after one side exposures would provide confidence that the approaches suggested herein are on the right track as well as information valuable for setting inspection intervals.

Now that there is a focus on role of internal methane pressure on shortening stress-rupture life, more effective test plans can be developed. Great benefit could be derived from planning tests wherein methane pressure, rather than hydrogen pressure, is the experimental variable. It is essential that this be done for each alloy of interest. The complex interaction of applied stress and methane pressure may differ among the alloys of interest.

All test programs should include, in addition to the usual microstructural characterization of the materials, a convenient measure of the availability or reactivity of carbon. The method might be something as simple as a separate test to measure decarburization rate or determining the amount of carbon left in solid solution after tempering/PWHT. Finally, monitoring of hydrogen diffusion through operating equipment is long overdue.

There are many things we have yet to learn. The few items listed here would provide a wealth of necessary information. The following are some thoughts about a test program and actions to be taken.

We now recognize that details of attack are sensitive to many variables. Conclusions about behavior of materials susceptibility should be based on tests at pressures and temperatures as close as practical to operating conditions. The insights gained in preparing this Technical Basis Document suggest the outlines of studies that might profitably be conducted to test the concepts

advanced herein and provide important information for Fitness-for-Service evaluation, inspection planning and risk based equipment management.

19.0 Overview and Conclusion

While there are many shortcomings with regard to the historical records of operating conditions that have led to attack the general trends and positions of the operating limit lines provided by API RP 941, have not been seriously called into doubt, aside from those provided for the 0.5% Mo steels.

The kinetics of the methane reaction suggests an explanation for the shapes of the curves in API RP 941. At temperatures above the “knee”, reactions may be rapid, equilibrium methane pressures can be reached if voids and cracks initiate. At temperatures below the knee, a pressure “plateau” is observed because rates of nucleation and methane formation are low.

The rate of methane formation in steel is expected to increase with dissolved hydrogen content, carbon content, temperature and the available nucleation sites for bubbles or fissures.

When temperature, hydrogen content and carbon activity in the steel produce methane at pressures in excess of the material’s tensile or creep strength, attack will proceed over a period of time. This concept was proposed years ago by many investigators.

Measurement of carbon activity in steel does not appear to be practical, but some reasonable estimates of the activity based on the literature, past performance and free carbon concentration are provided herein to enable estimates of methane pressure.

The methane pressures that may develop in cavities or cracks at the safe operating limits in API RP 941 appear to be consistent with material strength properties.

An approach has been developed whereby stress-rupture tests in hydrogen can be used as benchmarks to estimate isochronous failure curves for the hydrogen pressure-applied stress interaction.

Sophisticated void growth models (Annex G) are useful in explaining trends generally conforming to the curves in API RP 941. However, implementing the models requires numerous material properties that are not available and many assumptions that make quantitative implementation impractical at this time.

Simplified equations for reaction rate based parameters of the P_v and P_w type (Annex F) depict the trend of behavior of limited data for C-½Mo steel, upon which they were based. However, they are difficult to justify and implement for other low alloy steels.

Austenitic and ferritic stainless steel weld overlay or cladding can prevent or retard hydrogen attack by lowering hydrogen content in the backing steel. High-chrome ferritic steels are less effective than austenitic, but still potentially very helpful. The benefits of overlay or cladding decrease with increasing backing steel thickness (Annex D).

Progress in understanding hydrogen attack has been hampered by problems that are not easily overcome. These include the difficulties of measuring carbon activity, quantifying the degree of attack, characterizing microstructure (nucleation sites) and designing conditions for useful experiments. Available test results are not adequate to enable quantitative prediction of

behavior. Recent improvement in understanding the phenomenon should allow development of a test program to establish safe operating limits, a Fitness-For-Service methodology and a better understanding of issues needed for Risk-Based Inspection.

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