The Technical Basis Document for API RP 941

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Addendum 1

This addendum is comprised of two new annexes—Annex I and Annex J—and contains completely new information.

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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