

Looking Behind the Curtain of API RP 941 High Temperature Hydrogen Attack (HTHA) Data

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ABSTRACT

This paper will present an eye-opening look at some of the historic data and letters of correspondence that are the historical basis of the API RP 941 “*Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*” (a.k.a. The Nelson Curves). The focus of the paper is primarily on carbon steel and UNS K12320 (C-0.5Mo) data including information regarding the ‘removal’ of the C-0.5Mo curve in 1990.

In 2015, a significant change was made to the carbon steel curves in the 8th edition of API RP 941. It is the first change to the curves in the last 25 years. Based primarily on carbon steel failures that have come to light over the last 8 years, a new curve was added for Non-Post Weld Heat Treated (Non-PWHT) carbon steel. This new curve is approximately 50°F and 50 psia partial pressure H₂ below the existing carbon steel curve.

Some of the recent carbon steel failures that prompted the addition of the new Non-PWHT curve have been referred to as exhibiting non-classical HTHA damage morphology. A review of this damage morphology as well as other cases of similar damage of carbon steel and C-0.5Mo are included.

Key words: High Temperature Hydrogen Attack, HTHA, Nelson curve, Carbon Steel, C-0.5Mo, API RP 941, decarburization

INTRODUCTION

The selection and continued operation of materials of construction for piping and equipment operating in high-temperature hydrogen service have been guided by the “Nelson Curves” for over 65 years.¹ The Nelson Curves serve as empirical guidelines comprised of graphical plots establishing operating limits of temperature and hydrogen partial pressure conditions for carbon steel and low alloy steels. The data is a collection of reported HTHA failures; HTHA-damaged but non-failed components; and several cases of satisfactory operation. The plots are based on a collection of data from refineries and ammonia plants as well as laboratory experiments.²

G.A. Nelson originally published curves in 1949, 1958, and 1965 prior to the development of API RP 941.^{1,3,4} The 1949 curves were reported to have had more than 22 shifts prior to the first

publication.² An API Committee assumed responsibility for the document in 1965 after G.A. Nelson's 3rd publication, thereby creating API RP 941 "Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants", in 1970, the 1st edition.⁵

CHANGES TO THE RP 941 C-0.5Mo AND CS CURVES

C-0.5Mo

Over the life of the RP 941 document, several changes have been made to the curves. C-0.5Mo was included in Nelson's original curve in 1949, and was subsequently shifted upward (indicating better HTHA resistance) in 1965, and up again in 1970 when the API RP 941 1st edition was published, as shown in **Figure 1**.^{1,4,5} In 1977 (API RP 941 2nd edition), the C-0.5Mo curve was lowered due to incidents in the industry, and in the 3rd edition in 1983 a disclaimer about C-0.5Mo in catalytic reformers was overlaid on the figure cautioning its use.^{6,7} In the 4th edition in 1990, as a result of several additional industry failures, the C-0.5Mo curve was deleted from Figure 1 and moved to its own Figure 2, and in the 5th edition it was permanently moved to a separate annex as Figure A1.^{8,9}

Carbon Steel

The recent 8th edition of API RP 941 incorporates a new curve for welded and non-PWHT carbon steel.¹⁰ However, this is not the first time a welded carbon steel curve has appeared. In 1959, a curve for welded carbon steel was added to Nelson's second publication of the curves, which remained in API RP 941 1st edition.^{3,5} In API RP 941 2nd edition, only a single carbon steel curve was provided, overlapping the previous editions welded carbon steel curve. The change in position of these curves over time is shown in **Figure 2**.⁶

DETAILS OF DATA POINTS REPRESENTED IN API RP 941 CURVES PRIOR TO 2008

C-0.5Mo

The data set that currently comprises the API RP 941 C-0.5Mo curve, now in Appendix A1, is based on 39 owner/user submissions which account for a total of 71 points plotted on the graph. These include HTHA-attacked components (designated by shaded triangles) and HTHA non-attacked components (i.e., "satisfactory cases") designated by non-shaded triangles.

The last data point added to the C-0.5Mo Nelson Curve was in 1993, and was included in API RP 941 5th edition. All of the owner/user data submissions are supported by a report. These reports range in level of detail from minimal information to very detailed metallurgical analyses. For this paper, the historic data that was provided to API over the years is summarized and categorized as a function of thickness, exposure time, and other information as shown in **Figure 3** through **Figure 5**.^{2,9}

Although many cases of HTHA attack of C-0.5Mo piping and equipment have been reported to API, there are vast numbers of successful applications which are not documented and not reported. The mixture of success with C-0.5Mo can most likely be attributed to the variation in HTHA resistance related to differing base metal chemical composition, microstructure and heat treat condition (i.e., PWHT vs non-PWHT; and normalized & tempered vs annealed) that have been used in-service.¹⁰ Unfortunately, there is a noticeable lack of information in the API RP 941 database regarding these details.

Carbon Steel

The data set that comprises the API RP 941 carbon steel curve (dataset prior to 2008) is based on 22 submissions from owner/users that account for 52 points on the API RP 941 carbon steel curve. Unfortunately, 13 of the 22 submitted reports (10 data points) have been lost to posterity.⁹ Two of

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