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Sour or Not Sour? That Is the Question:

A Review of The NACE “Sour Limit” – Evolution and Implications for Modern Oil & Gas Production

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ABSTRACT

The use of 0.05 psi H₂S partial pressure as the threshold determining when sulfide stress cracking (SSC) resistant materials are needed was codified in NACE MR 0175 (1975) nearly a half century ago and has served the industry well since implementation. The origins of this pressure are empirical and largely forgotten but there is significant history showing that it is a safe, conservative limit. As the oil and gas industry continues to innovate and mature, it is imperative to maintain knowledge of the basis of the sour limit and how it may be applied.

Key words: Corrosion science and technology, hydrogen sulfide, standardization.

INTRODUCTION

For the past 70 years, H₂S and its associated cracking mechanisms have been investigated, limits developed, and material properties identified. Prior to 1975 there were no standards, but there were standardized requirements outlined in various NACE ⁽¹⁾ regional and national documents, in particular NACE 1F163 and 1F166, which were the precursors to NACE MR0175 (Wellheads and Trees). Some materials properties, notably the 22 HRC hardness limit had been notionally recommended in these early reports but were not formally standardized until NACE MR 0175 was issued in 1975.¹⁻³ When NACE MR 0175 (1975) was issued, the materials requirement focused on acceptable material properties for wellhead and tree materials since they involved the largest perceived safety risks.

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Setting a threshold when an environment should be considered sour or not was not included in NACE MR 0175 (1975) but was under prior industry consideration based on Texas Statewide Rule No. 36 which used 100 ppm H₂S in the flow stream as a limit. API ⁽²⁾ 14E (1975) noted a limit as 0.05 psia H₂S partial pressure or greater than 15 ppm (mg/L) H₂S in the aqueous solution as a sour/non-sour threshold.⁴ The table from API RP 14E (1975) with this information is provided in Table 1. The 0.05 psia (0.345 kPa) H₂S partial pressure was adopted by NACE MR 0175 in the 1978 edition as the sour/non-sour threshold. The 15 mg/L H₂S limit was not carried forward in MR 0175 and is considered more permissive for H₂S content as 0.05 psia (0.345 kPa) H₂S would translate into approximately 10 mg/L H₂S at ambient pressure in a low salinity aqueous phase; higher pressures or salinity would result in even less dissolved H₂S.

Table 1
General Guide for Materials for Resistance to Sulfide Stress Cracking
(Adapted from Table 1.2 in API 14E 1975) ⁴

H ₂ S Partial Pressure	H ₂ S Concentration in Aqueous Solution	Required Material Specification	Maximum Hardness of Acceptable Carbon, Low, and Medium Alloy Steels
(psia)	(ppm or mg/L)	-	(HRC)
greater than 0.05	greater than 15	NACE MR-01-75	22
0.01 – 0.05	3 – 15	*	*
less than 0.01	less than 3	API, ASTM, etc.	**

* There are no industry standards covering these conditions. Operators should specify materials for these conditions based on experience and data, taking into full account the significant variables of the application: design stress, stress concentrations, temperature, pH, etc.

**Hardness resulting when manufactured in accordance with normal specifications.

When NACE MR 0175 was updated in 1978, the 0.05 psia (0.345 kPa) H₂S partial pressure sour/non-sour threshold was adopted with the caveat of the H₂S having to be “in the gas phase”. While simplistic, many of the wells that produced H₂S had a gas phase where the partial pressure could be readily calculated from a gas phase sample.⁵ This threshold is still used today. While no written evidence specifically supports the 0.05 psia (0.345 kPa) H₂S partial pressure sour/non-sour threshold other than inference from laboratory data and association from field experience, it has successfully and safely protected personnel, the environment, and the industry since adoption over 40 years ago. The lack of change and continued adoption by other standards and regulations further supports the validity of the 0.05 psia (0.345 kPa) H₂S limit.

ORIGINS OF THE 0.05 PSIA (0.345 kPa) H₂S PARTIAL PRESSURE THRESHOLD

During the early investigations into understanding SSC, many parameters were investigated to increase the understanding the cracking susceptibility of materials in oil and gas production environments. Hence, material properties such as yield strength, tensile strength, and hardness were investigated along with metallurgical processing, chemical composition, and microstructure. Environmental variables such as pH, H₂S concentration and temperature were also investigated to determine key parameters and those were incorporated in the developing testing procedures.

Much of the early testing in the 1950’s and 1960’s was on API 5AC, now 5CT, J55, N80, and P110 grades of oil country tubular goods (OCTG). Testing was also performed on many other compositions of OCTG used at that time, such as 5Ni, 9Ni, and 7Cr. These tests were primarily driven by a need to determine what materials would not crack when exposed to H₂S and required for the new test methods

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being developed. The majority of test methods and testing performed at the time were at ambient pressure and temperature.⁶⁻¹⁰ Some of these test methods were later standardized in 1977 within NACE TM0177.¹¹

One of the best examples of the work being done at this time is provided by Treseder and shown in Figure 1 for P110 and 9Ni with the 0.05 psia (0.345 kPa) H_2S partial pressure threshold superimposed.¹² P110 and 9Ni were specifically selected as two materials known to be more susceptible to SSC in sour service based on field experience so that a threshold could be determined. The bent beam test protocol and specimens used eventually became NACE TM 0177 Method B and a stress concentration (S_c) of 10 was selected for acceptability. Results indicated that these two materials known to be susceptible to SSC could safely be used if the H_2S partial pressures was 0.015 psia (0.001 atm or 0.1 kPa) in the gas phase at room temperature or less based on this criterion. Tuttle later acknowledged that a transition in susceptibility based on Shell testing was between 0.015 psia (0.001 atm or 0.10 kPa) and 0.15 psia (0.01 atm or 1.0 kPa) H_2S partial pressure, and this partial pressure once determined could be used to define a safe threshold for H_2S ; a sour/non-sour threshold.¹³

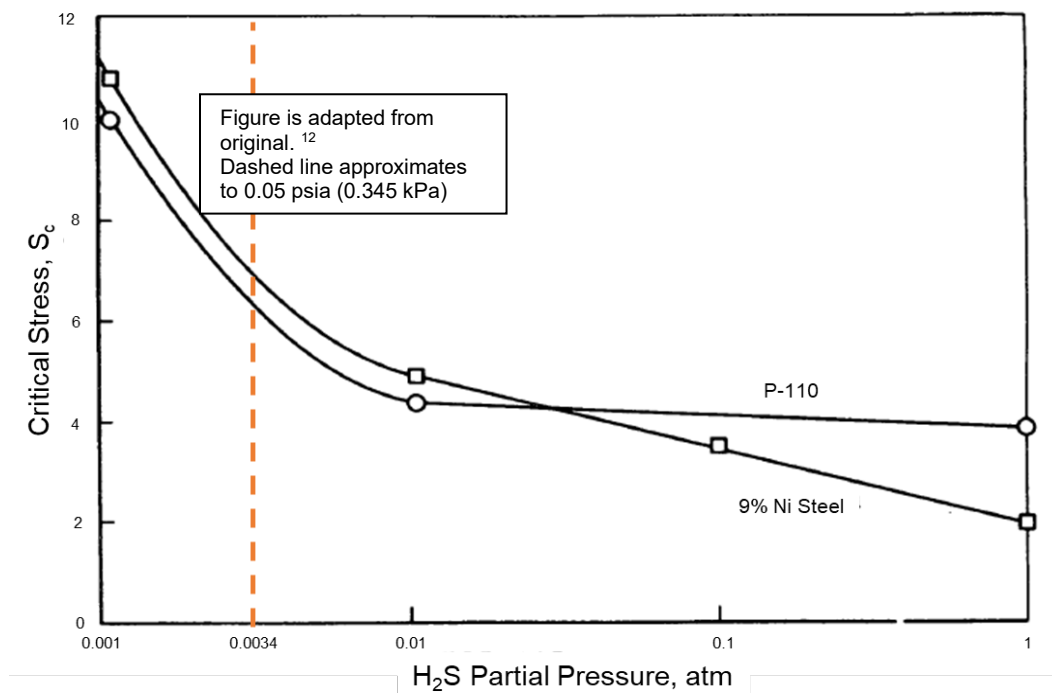


Figure 1: Early SSC Results for P110 and 9Ni

Understanding of SSC susceptibility on OCTG continued using a variety of test methods continued into the 1970's when standardized, and more alloys including AISI ⁽³⁾ 410 stainless steel and very high strength carbon steels such as V140 and V150 grades were investigated in additional many other grades and compositions.¹⁴⁻¹⁷

Two of the better examples from the results of these works are provided in Figure 2 and Figure 3 by Kane et al., which were based on notched C-rings (a modified NACE TM0177 method C) tested at ambient pressure and temperature. The 0.05 psia H_2S (0.345 kPa or 0.34 mol%) partial pressure sour/non-sour threshold is superimposed on both for reference. When the 0.05 psia (0.345 kPa) H_2S partial pressure sour/non-sour threshold is compared against these results, there is good alignment

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with field experience for what materials are considered applicable for sour service, which are not, and which have limited use based on today's understandings. Among these are:

- P110: routine use should be in non-sour applications, but some resistance to SSC is possible.
- SOO-125 (now Q125): less resistance to SSC than P110, but some resistance under more select conditions than P110.
- AISI 410: some acceptability for limited H₂S exposure, but not as much as carbon and low alloy steels of similar strength or lower.
- V150: susceptibility to H₂S cracking mechanisms under all conditions.

The susceptibility of the higher strength low alloy steel grades, such as V150, led to incorporation of a warning note for the suitability of materials with yield strength above 140 ksi in the non-sour region.

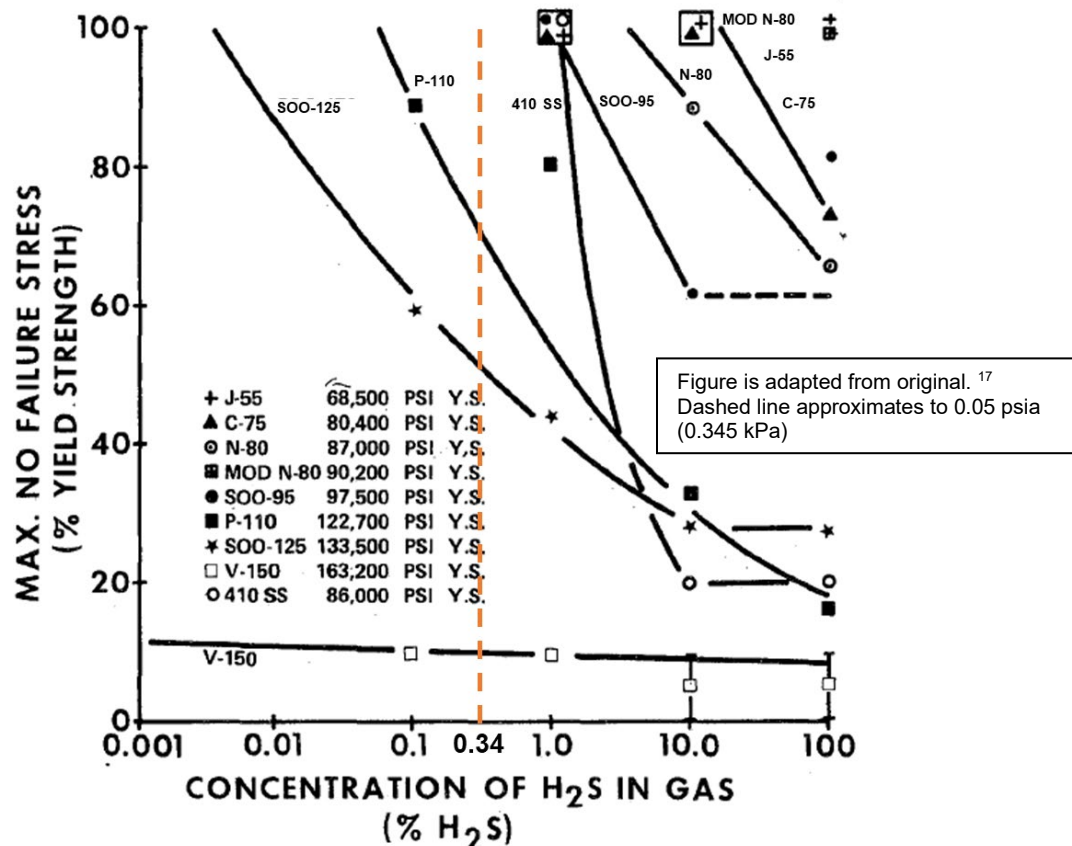


Figure 2: SSC Susceptibility Based on Loading

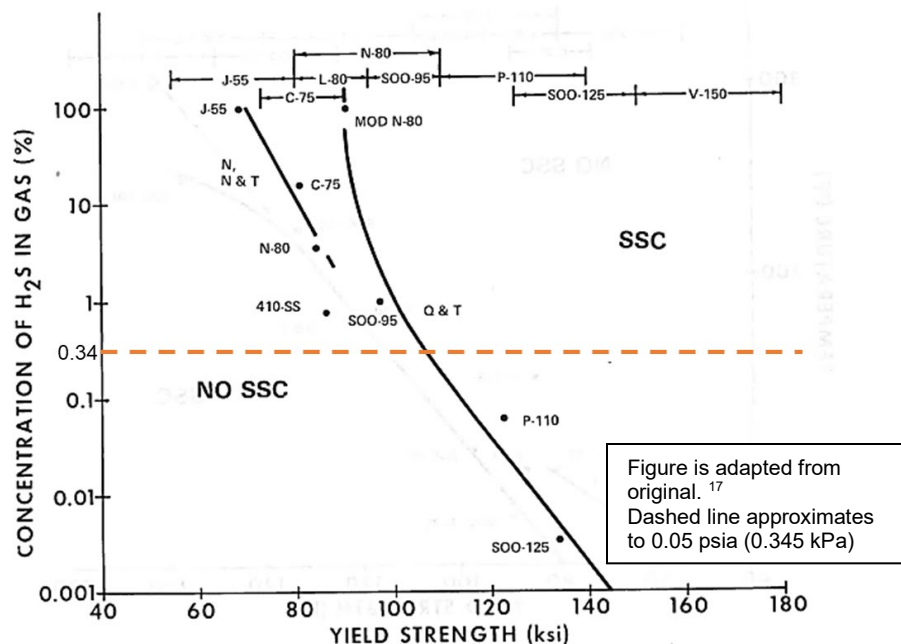


Figure 3: SSC Susceptibility Based on Grade

Additional work was done to align test results from earlier studies, better define material limitations, and develop standards.^{18,19} A round robin evaluation was also conducted to determine how reproducible smooth tensile test specimens and notched beams loaded in deflection were at determining if materials were susceptible to SSC using procedures from NACE T-1F-9, the committee that developed NACE TM 0177.^{11,20} The round robin program noted that there was scatter in the SSC data, in many cases resulting from variations in laboratory procedures being used in various laboratories at the time for maintaining the ambient environment and stressing of the specimens. This information was used to develop more reproducible tensile test procedures as ultimately standardized in NACE TM 0177. At the same time, laboratory investigations were being conducted that investigated the veracity of the empirical field observations that elevated service temperatures (as observed downhole) had a mitigating effect on SSC susceptibility particularly in higher strength API casing grade steels (e.g. P110 and higher). Data generated in the reference study gave a clear technical basis that, in fact, higher strength and normally SSC-susceptible steel components could be used downhole provided that certain minimum temperatures could be maintained during production and shut in.¹⁷

PARTIAL PRESSURE OR FUGACITY?

Much of the early testing publicly presented does not provide details on the specifics regarding pressure, and only a few specifically report the total pressure. Many of these tests were performed based on the NACE T-1F-9 proposed test method, the precursor to NACE TM 0177, and while not specifically stated, are considered to have been performed at atmospheric pressure based on the test method. Photos of the test setups used provides further support of this as they were often glassware or a polymer vessel and tested with H₂S saturated gas.^{6,14,20-21} Other test data was gathered under similar conditions with elevated temperatures, but the temperature was maintained sufficiently less than 212°F (100°C) so that boiling did not occur, and evaporation could be minimized. These tests are also considered to have been performed at atmospheric pressure. A few early published tests did state the test pressure as atmospheric with some providing the partial pressure associated with testing.^{6,7,12,17,25}

H₂S fugacity (f_{H_2S}) was recognized as a better approximation to indicate cracking susceptibility during the early sour gas developments at higher pressures in the 1970's as it explained some of the gaps between laboratory testing and field experience, but it was not significantly investigated as the majority