

Development of the NACE “MR-01-75” and NACE “TM-01-77” Standards: Part II – Accelerated Material Qualification Testing in Sour Environments at Near Atmospheric Pressure

Brent W.A. Sherar
Honeywell Connected Enterprise
11201 Greens Crossing Blvd.
Houston, TX 77067
USA

Eric Caldwell
GATE Energy
13501 Katy Freeway Suite 3300
Houston, TX 77079
USA

Peter F. Ellis II
Honeywell Connected Enterprise
11201 Greens Crossing Blvd.
Houston, TX 77067
USA

Russell D. Kane
iCorrosion LLC
1221 Willard Street
Houston, TX 77006
USA

ABSTRACT

This paper is Part II of a two-part series intended to narrate the history, some of which has been forgotten over time, leading up to the publication of the first Material Requirement (MR-01-75) standard prepared by NACE and its subsequent auxiliary standards. Previously, Part I described the field observations and discussed the metallurgical factors that were being investigated by the historical NACE T-1B and 1F committees to support the development a sour service materials standard. In Part II, we focus on the rationale behind the use of accelerated laboratory test procedures and their development to differentiate metallurgical behavior in sour environments. The original sulfide stress cracking (SSC) test methodologies would later be codified as a Test Method in NACE TM-01-77 (1977).

A review of the historical events culminating in NACE MR-01-75 and NACE TM-01-77 provides a technical basis for the historical use of NACE Solution A (5 wt% NaCl + 0.5 wt% acetic acid) to evaluate metallurgical factors, and the origins of several common SSC NACE Test Methods still used today: A (tensile), B (three-point bent beam), and C (C-ring). The accelerated laboratory test results, in combination with parallel field trials (performed in advance of the first NACE MR-01-75 publication), supported the ≤ 22 Rockwell C (22 HRC) hardness limit for carbon and low alloy steels in sour environments containing ≥ 0.05 psia H_2S partial pressure. As the oil and gas industry continues to innovate and mature, it is imperative to maintain knowledge of the origins of the NACE MR-01-75 and TM-01-77 standards and their intended purposes.

Key words: NACE MR-01-75, NACE TM-01-77, sulfide stress cracking, hydrogen sulfide, atmospheric pressure, corrosion science and technology, standardization

Introduction

This paper is Part II of a two-part series intended to narrate the history, some of which has been forgotten over time, leading up to the publication of the first Material Requirement (MR-01-75) standard prepared by NACE and its subsequent auxiliary standards. Previously, Part I¹ described the field observations and discussed the metallurgical factors that were being investigated by the historical NACE T-1B and 1F committees to support the development a “harmonized” sour service materials standard. In Part II, we focus on the rationale behind the use of accelerated laboratory test procedures and their development to differentiate metallurgical behavior in sour environments. The original sulfide stress cracking (SSC) test methodologies would later be codified as a Test Method in NACE TM-01-77 (1977).

The inspiration for writing Part II was to answer a fundamental question regarding sour service standards: “Under what test conditions, and with which specific methodologies, were used to establish the original 0.05 psia (0.3 kPa) H₂S criterion?” The authors decided to independently review the historical SSC research performed during the 1950s to 1970s, the pivotal period preceding the publications of the original NACE MR-01-75 and NACE TM-01-77 standards to provide historical context to the above question and rationalize several other material requirements. In Part II, the focus is on the accelerated laboratory test methods used to evaluate SSC susceptibility of carbon and low alloy steels.

Recently, Caldwell *et al.*² provided an overview of some of the early research on SSC testing and documented that the origins of the ‘sour service’ definition (0.05 psia [0.3 kPa] H₂S partial pressure). The definition is based on testing under “ideal gas”/atmospheric lab conditions, not those of the reservoir or field.³ In addition, both Caldwell *et al.*² and Sherar *et al.*^{4,5} explain the progression from historically using simple H₂S partial pressure (P_{H₂S}) calculations to assess severely sour wells (> 1 mol % $\equiv$ 10,000 mol ppm H₂S) to the modern approach of utilizing sophisticated non-linear thermodynamic models to evaluate modern production environments. Predicting sour severity of modern, mildly sour HPHT wells either by thermodynamic fugacity-based⁶ or aqueous concentration-based⁵ approaches are gaining industry acceptance, because, while many production zones are now routinely deeper (i.e., higher total pressures), many offshore wells contain relatively low mole fractions of H₂S in the gas/hydrocarbon phase (e.g., y_{H₂S} < 100 mol ppm). Correcting for non-ideal thermodynamic effects has been demonstrated to reduce over conservatism when modeling mildly sour HPHT wells.^{4,5,7-13} With the recent publication of ISO 15156-1:2020,¹⁴ equipment users are now permitted to use either fugacity, activity, or dissolved aqueous concentration as alternative sour severity metrics, with the proviso that these thermodynamics parameters are validated via physical testing, which may allow equipment users greater flexibility in material selection and design.⁵

In this article, the choices made by early researchers when designing “standard” laboratory test methods to evaluate SSC of carbon and low alloy steels are rationalized.¹ By documenting the past, we hope to both educate those entering the field and provide a rationalization for where the “22 HRC” / “1% Ni” (in Part I) and “0.05 psia (0.3 kPa) H₂S” (in Part II) criteria were derived from. This paper will also demonstrate to users of the current ISO 15156-1:2020 Standard¹⁴ on why the above policies are still applicable today nearly 50 years after their original adoption. Only by documenting the events that led to the adoption of the above criteria can an informed decision be made to potentially revise those policies, which are still referenced in the latest edition of the Standard,³ if so desired.

Although the original SSC testing references are cited throughout this article, please note that most of the papers cited in this review article can be found in the “blue book” edited by Tuttle and Kane titled *H₂S Corrosion in Oil & Gas Production – A Compilation of Classic Papers*.¹⁵ It is an excellent anthology and resource for current and former members of the IOGP 15156 community to consult.

¹ At the time of development, the test methods were designed with the intention to qualify materials under severely sour lab conditions, so that the material/equipment could be deployed in any sour environment.

BACKGOURND

On Sunday, February 5, 1975, a 410 stainless steel valve from a sour gas injection well ruptured releasing H_2S into the atmosphere. The sour gas (comprised primarily of 4 mol% H_2S and 95 mol% CO_2) slowly migrated approximately 200 ft towards a nearby home located about 3.5 miles northeast of Denver City, TX. Tragically, this event led to nine fatalities: Eight civilians and one oilfield worker. The Denver City fatalities, in conjunction with several other material failure events that occurred at around the same time, increased the total number of statewide fatalities to 17 within a short four-month period.¹⁶

In March 1975, NACE published the first edition of MR-01-75 titled “Materials for Valves for Resistance to Sulfide Stress Cracking in Production and Pipeline Service.” This Standard replaced NACE Publications 1F166 (1973 edition) and 1B163. In the 1975 edition of NACE MR-01-75, the Standard specifies for carbon and low alloy steels (LAS) valve components, a hardness limit of ≤ 22 Rockwell C (22 HRC) for equipment used in sulfide-containing sour environments. The 1975 edition, however, did not numerically define which environments were deemed sour.

Collectively, the above incidents compelled the Railroad Commission of Texas (RRC) to issue Statewide Rule 36 “Hydrogen Sulfide Safety”, which regulates the safe use handling of H_2S at well sites. In addition, the RRC notified the industry to define sour limits for *all* oilfield components to ensure material integrity or limits would be defined by the regulator.

To address both regulatory requirements and provide clear guidance to equipment users to avoid incidents like Denver City in the future, NACE MR-01-75 was revised in April 1978 to cover all oilfield materials and included the H_2S partial pressure ($P_{\text{H}_2\text{S}}$) ≥ 0.05 psia (0.3 kPa) criterion, which was applicable to all metallurgies.^{17, 18} Later, NACE MR-01-75 was subsequently revised in 1979 and 1980 as new materials were added to the Standard.

A thorough review of the available literature reveals that the ‘0.05 psia H_2S ’ criterion was an empirically derived value, established primarily from the results of both field¹⁹⁻²¹ and laboratory²²⁻²⁴ SSC tests conducted on what were known at the time as acceptable and non-acceptable steels during the 1950s to 1960s. The architects of the original NACE MR-01-75 standard²⁵ were well aware that SSC was the result of the combination of three requirements: 1) Susceptible metallurgy; 2) sufficient applied stress; and 3) adequate environmental severity.

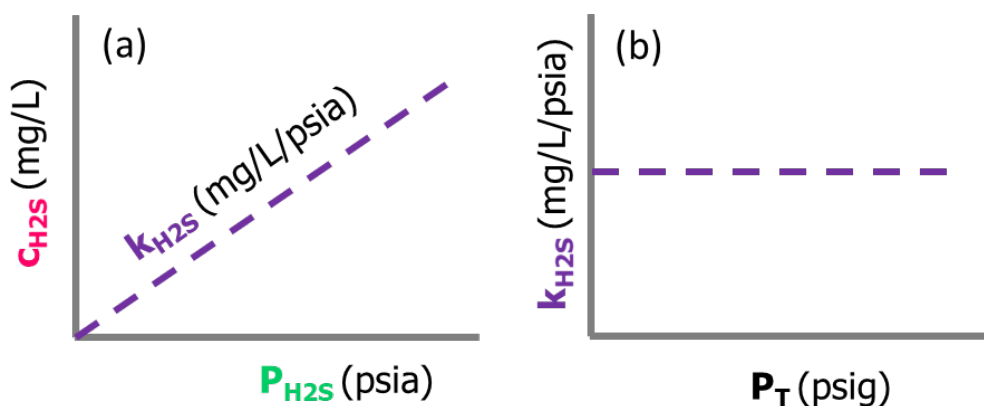


Figure 1. Historical H_2S solubility assumptions based on the $P_{\text{H}_2\text{S}}$ Paradigm.⁴

Historically, when qualifying carbon and low alloy steels for sour service at room temperature, stressed specimens were immersed in acidic solutions containing up to 5 wt% NaCl and purged with either pure H_2S at 14.7 psia (101.3 kPa $\equiv$ 1 atm) or H_2S in mixed gases to obtain $P_{\text{H}_2\text{S}} < 1$ atm.^{23, 24} In order to evaluate metallurgical factors that contributed to SSC, early researchers eventually settled on a test

solution containing 0.5 wt% acetic acid with or without 5 wt% NaCl.⁽²⁾ It was revealed that susceptibility to SSC was influenced by H₂S present in acidic solutions for certain carbon and low alloy steels at different hardness values. Under the above test conditions, an apparent H₂S solubility coefficient (k_{H_2S}) of ~200 mg/L/psia ($\equiv$ 0.87 mol/L/atm) is predicted.

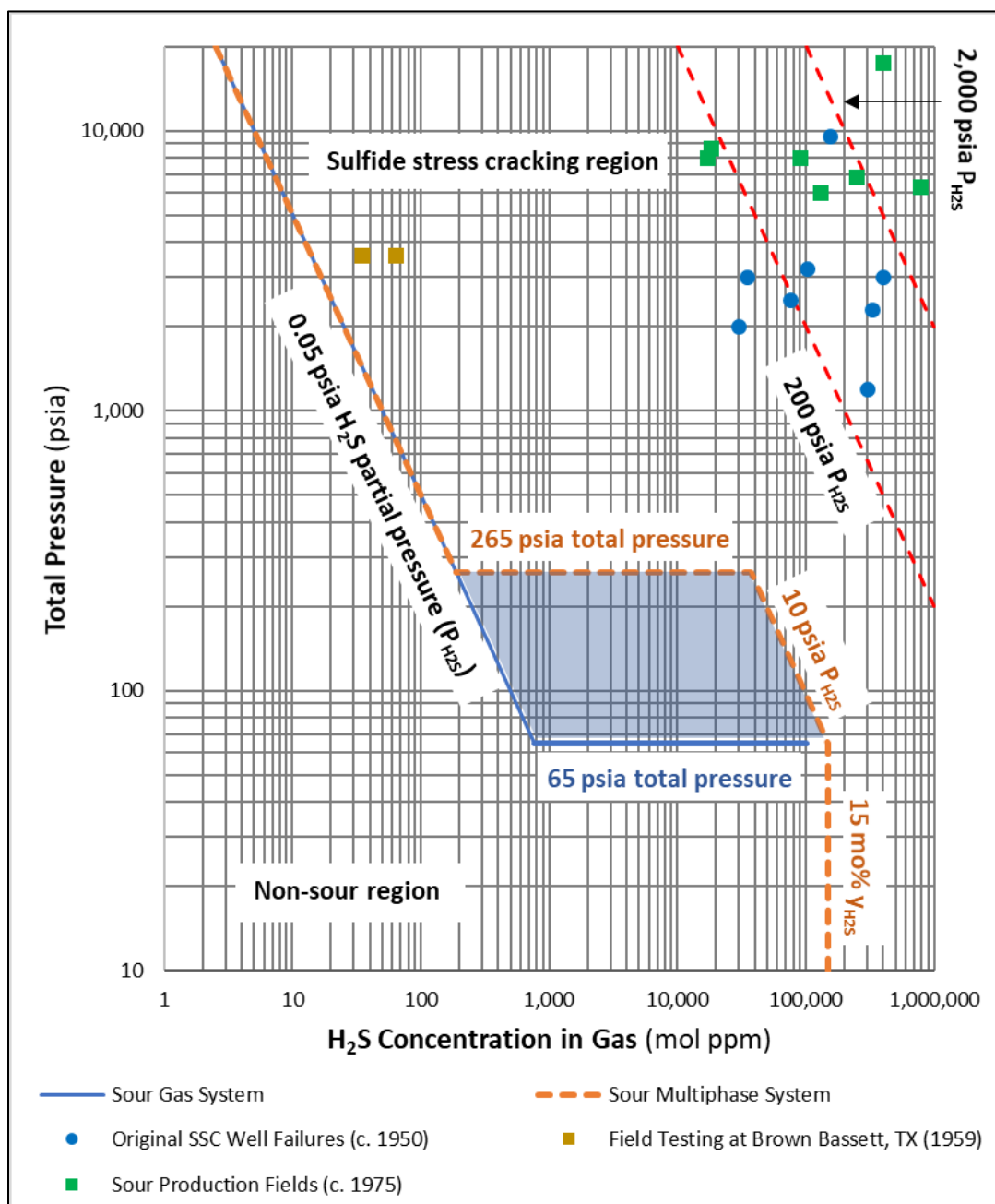


Figure 2. Sour gas and multiphase systems domain diagram; reproduced from NACE MR 01-75 (Revision 1980). Superimposed on the diagram are the sour field environments investigated during the development phase of the original Standard.²⁵ (Refer to the Appendix Table A.1.)

⁽²⁾ This was a “one size fits all” test solution intending to give a reasonable worst case approach to solving H₂S resistant material selection. The successful application of this approach led to the standardization of ‘NACE Solution A’, composed of 5 wt% NaCl + 0.5 wt% acetic acid, into NACE TM-01-77.

Based primarily on the atmospheric laboratory results, it was assumed that ideal gas behavior governed over the entire total pressure range for all oil and gas systems implying that the C_{H_2S} - P_{H_2S} relationship increases linearly with increasing P_{H_2S} with a constant slope of k_{H_2S} (Figure 1a). Thus, k_{H_2S} (the “ideal” H_2S solubility [i.e., Strict Henry’s Law] constant) is independent of increasing total pressure (P_T) (Figure 1b). These assumptions were considered reasonable in 1975, because P_{H_2S} is a relatively accurate approximation for C_{H_2S} at room temperature and low total pressures for dilute solutions. Thus, for both sour gas and sour multiphase systems, the $P_{H_2S}=0.05$ psia isobar was linearly extrapolated from near atmospheric pressure to 10,000 psia (as shown in Figure 2).

According to the 1978 edition of NACE MR-01-75,²⁵ the $P_{H_2S}=0.05$ psia criterion was only applicable for sour service environments where the total pressures were > 65 psia and > 265 psia for sour gas and sour multi-phase systems, respectively. At the time of publication, a lower total pressure boundary (below which, no material restrictions were required) was justified for the following reasons: 1) Low pressure rated systems were exempt as “off-the shelf equipment normally used for sweet gas provided adequate service;”²⁶ 2) Materials that were used at the time for low total pressure applications were mostly in available in lower hardness/yield strength grades²⁷ and thus not expected to be prone to SSC; and 3) No SSC failures were reported during the lead up to the publication of the 1978 edition of NACE MR-01-75.²⁶

It is important to note that, as shown in Figure 2, a gas system operating at 65 psia was only considered sour if the gas phase contained a minimum of $y_{H_2S}=769$ mol ppm. Whereas, for a multiphase system operating at 265 psia required a minimum of $y_{H_2S}=189$ mol ppm. To achieve the equivalent P_{H_2S} threshold of 0.05 psia in the lab at atmospheric pressure, a minimum of $y_{H_2S}=3,400$ mol ppm in the gas phase is required. Based on field observations¹⁹ and laboratory testing results,^{24, 28} SSC susceptibility appeared to be dependent on P_{H_2S} in combination with an acidic aqueous phase. Therefore, at the time, it was assumed that field sour severity could be directly replicated in the lab based on matching the P_{H_2S} without considering changes in H_2S solubility (k_{H_2S}) with total pressure, which Sherar *et al.* termed the ‘ P_{H_2S} Paradigm’.⁴ In other words, it was assumed that the ideal gas law was applicable to describe the phase behavior of H_2S at both near atmospheric pressure (lab) and elevated operating pressures (field). For systems operating at low total pressures, or for severely sour fields, the premise that atmospheric laboratory tests can be designed merely by decreasing the total pressure and increasing y_{H_2S} to maintain the *same* P_{H_2S} expected in the field and yield an *identical* SSC outcome for the same oilfield material was reasonable and has historically served the industry well.⁽³⁾

ORIGINAL SSC LABORATORY TESTING PRECEDING NACE “MR-01-75” AND NACE “TM-01-77”

Environmental Severity of the ‘Classic’ SSC Atmospheric Laboratory Test

The primary objective of researchers in the 1950s to 1970s was not to replicate the “real” sour phase behavior expected for an actual wellbore during sour qualification of candidate materials,^{29, 30} but rather to select relatively severe (reasonably “worse case”) laboratory environments for evaluating metallurgical factors.^{23, 24, 30, 31} The motivation for testing was to determine the minimum applied stress (often reported as a percentage of yield strength) to avoid brittle failure by SSC in the field.³⁰ In order to obtain failures of relatively resistant materials in a reasonably short period of time (within 30 days), test conditions were purposely made severe in terms of:

- (1) selecting high yield strength (YS) materials with high hardness values;
- (2) machining stress raisers/concentrators (e.g., notched) specimens;
- (3) stressing/straining the specimen beyond its actual YS;

(3) This assumption only becomes incompatible when applying the relationship to systems at high total pressures under mildly sour environmental conditions, where non-ideal thermodynamic effects cannot be ignored, and trying to maintain reasonable levels of “conservatism” for material qualification.^{5, 6}

- (4) immersing the stressed specimen in a test solution, artificially made more acidic than expected under normal production conditions (e.g. pH <3.0 versus pH 3.5-5.0); and
- (5) purging the test solution with a gas containing high concentrations of H₂S.^{23, 30, 31}

In an attempt to simplify laboratory test procedures and increase screening capacity, SSC testing was primarily conducted at atmospheric pressure. For convenience, materials were usually evaluated at room temperature in either pure H₂S at 1 atm or H₂S in mixed gases to obtain P_{H₂S} < 1 atm.^{23, 24} Such a high P_{H₂S} was justified as the original well failures in the late 1940s to early 1950s contained a gas phase with y_{H₂S} > 3 mol%,^{20, 21} while many wells being developed in the 1970s were expected to produce high levels of H₂S (y_{H₂S} = 1.25 to 78 mol%) and in some instances they were expected to co-produce elemental sulfur (refer to Table A.1 in the Appendix for details). It is important to recognize that the original SSC test methods, later standardized in NACE TM-01-77, and the material requirements specified in NACE MR-01-75, were designed to verify that a specific API-material grade, regardless of manufacturer, would not fail by SSC in the field. Again, the objective was not to replicate any specific field environment, but rather use a generic/pseudo production environment to evaluate metallurgical factors at near atmospheric total pressure.⁽²⁾

Table 1. A description of the test types used to evaluate the relationship between metallurgical properties and SSC during the 1960s.

Reference	Test Type	
	Specimen Geometry	Applied Stress/Strain
Blount et al., 1962 ³²	Notched C-ring: 0.25" W x 0.10" WT. A standard 45° Charpy V notch 0.015" deep with a 0.010" radius	130 % of yield deformation ⁽⁴⁾ ^a
Greco and Wright, 1962 ²²	Notched-Three Point Bent Beam (TPBB) coupons: 1/4" W x 3" L x 0.06" WT with 60° V-notch (20% of the coupon thickness) scribed along the short axis on one side	130% of the minimum yield stress
Hudgins et al., 1966 ²³	Notched C-ring: 0.25" W x 0.15" WT. 45° Charpy V notch 0.023" deep with 0.010" radius	130 % of yield deformation ^(Error! Bookmark not defined.) ^a
Treseder and Swanson, 1968 ²⁴	TPBB coupons with two drilled holes: 3/16" W x 3" L x 1/16" WT with two No. 60 drill holes at mid-section	Not specified ^b
Notes: a. Yield deformation was determined as the point of linearity departure from load-displacement curves on C-rings of the same material. ²³ b. Stress values were calculated using a simple beam formula. Authors ignored the stress concentration associated with the holes. Consequently, the yield point was likely exceeded in certain cases. Stress concentrations associated with these holes exceeded the yield strength of the material. ^{24, 33}		

Carbon and Low Alloy Steels Evaluated in SSC Tests During the 1960s

Testing in the 1950s to 1960s was performed over a wide range of oil country tubular goods (OCTG), from H-40 to P-110.^{19,22,23,24, 32, 34-37} While many of the grades were standard, some were heat treated so

⁽⁴⁾ If 130% of yield deformation was determined based on elastic bending, the value is approximately equivalent to the 0.2% offset strain on a smooth tensile specimen since post yield deflection are no longer linear with respect to stress and strain or load vs. displacement. This was later taken into account in the "modern" NACE TM0177 C-ring test methodology before it was common to strain gauge specimens as it is now.

that the yield strength varied from 49.5 ksi (341 MPa) to 175 ksi (1200 MPa) and hardness values ranging from 82 HRB to 40 HRC. A few non-standard compositions, such as 9% Ni and 9% Cr were also tested.

Test Types Used to Evaluate SSC for Carbon and Low Alloy Steels

Table 1 lists the various specimen geometries and applied stress/strain/deformation levels used to evaluate metallurgical properties during the 1960s. Candidate materials that were evaluated for SSC were either machined as C-rings (precursor to TM0177 Test Method C, but frequently notched) or three point bent beam coupons with or without stress concentrators (TPBB, Test Method B).^{23,24}

The severely stressed specimen design was justified as standard “buttress” coupling systems at the time were normally stressed at or above the yield strength when made up to specified leak-tight torques.²³ Regardless of the test type selected, the mechanical loads applied were considered a “reasonable” worst-case design scenario.

It is also worth noting that Bloom in 1955 was the first author to utilize the tensile specimen geometry to evaluate SSC of low alloy (e.g., J55 and N-80) and hardenable stainless (including 410 and 17-4PH) steels, with the main advantage that a precise tensile stress could be applied to the specimen.³⁶ The tensile geometry was later modified by Baldy in 1961 by straightening and lengthening the reduced section to fit in a glass cell “test jacket” containing a corrosive environment.³⁸ Baldy’s proposed test method³⁸ appears to form the basis of the original SSC test method later formalized in NACE TM-01-77.³⁹

Table 2. A description of the environmental parameters used to evaluate the relationship between metallurgical properties and SSC during the 1960s.

Reference	Environmental Parameters						
	Location	Temp. (°F)	Total Pressure	Gas Phase	Aqueous Phase	pH	Test Duration
Blount et al., 1962 ³²	Field testing at Brown Bassett Field, TX	90	3600 psia	Produced gas (56 mol% CO ₂ , 43.7 mol% CH ₄ , and 0.25 mol% C ₂ H ₆)	Not specified; assumed 5 wt% NaCl	3.0	27, 52, 85 days
Greco and Wright, 1962 ²²	Laboratory	RT	Atm.	H ₂ S in CO ₂	400 mg/L Cl ⁻	3.9	72 hours
Hudgins et al., 1966 ²³	Laboratory	RT	Atm.	H ₂ S in 5 mol% CO ₂ + bal. N ₂	5 wt% NaCl	4.5	up to 5100 hours (212.5 days) ^a
Treseder and Swanson, 1968 ²⁴	Laboratory	RT	Atm.	H ₂ S in N ₂	0.5 wt% acetic acid ^b	2.8	up to 98 days
Notes: a. Results helped to establish 720-hr (30-day) testing criteria. b. The TPBB method typically involved an acidic test solution without chloride to reduce the corrosion rate on very thin TPBB specimens.							