

A Review of Fit-for-Purpose Sour Tests of Low Alloy Steels: Effects of Buffer Chemistry and Purge Gas Composition

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ABSTRACT

Oil country tubular goods (OCTG) are routinely evaluated for sulfide stress cracking (SSC) resistance. Historically, most qualifications relied on full sour, i.e. 1 bar H₂S, to assure sour grades of OCTG for service in the field. Over the past two decades, it has become more routine to evaluate SSC resistance of OCTG, often higher strength grades, using fit-for-purpose (FFP) conditions. The practice of FFP testing of low alloy steels has evolved from methods outlined in EFC⁽¹⁾ 16 to NACE⁽²⁾ (MR0175/ISO³15156 - TM0177) and API⁽⁴⁾ 5CT. This paper reviews the original practices outlined in EFC 16 and the current range of practices used in industry with regards to the technical validity and conservatism of evaluations performed.

Key words: H₂S, sour, sulfide stress cracking, acetate buffer, OCTG, MR0175, TM0177, DCB

INTRODUCTION

Oil country tubular goods (OCTG) are utilized in well construction and completion in the oil and gas industry primarily to enable the flow of hydrocarbons and provide barriers between those fluids and the external environment. Resistance to environmentally-assisted cracking (EAC) is required in order to maintain the integrity of the OCTG for these reasons. For carbon and low alloy steel (LAS) OCTG

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materials, the dominant EAC concern is sulfide stress cracking (SSC), caused by hydrogen embrittlement in low pH H₂S-containing aqueous conditions in the well. Historically, most qualifications relied on so-called full sour tests, i.e. with 1 bar H₂S, to assure sour grades of OCTG for service in the field. Over the past two decades, it has become more routine to evaluate SSC resistance of OCTG, often higher strength grades, using fit-for-purpose (FFP) conditions that typically contain less H₂S and higher pH values compared to the historical “full sour” conditions.

The need for “milder” test conditions stemmed from the need to qualify grades of Cr-Mo OCTG with higher strength and hardness and accompanying lesser sour resistance compared to API grades L80 or T95. The basis for these “milder” condition evaluations included both FFP tests for defined well exposures and validation, or acceptance, testing of high-strength grades, such as C110, now an API-defined grade¹. Early examples of FFP testing are detailed in NACE Paper No. 04109 and Paper No. 05086 where C110 was tested in three different “mild sour” conditions as defined in Table 1 and four different “mild sour” conditions as defined in Table 2, respectively^{2,3}. As shown, the tests were done using a solution with 4 g/L sodium acetate buffer in the case of Paper 04109 and without buffer in Paper 05086; both sets of experiments used CO₂ balance gas for the H₂S purge gas. Testing was altered slightly for validation testing using mild sour conditions where 3.8% H₂S or 7% H₂S with N₂ balance gas were common². N₂ balance gas was primarily used as a convenience as a gas cylinder with N₂ balance gas contains approximately 5 times as much gas as one with CO₂ balance gas.

Table 1
Test Matrix for C110 FFP OCTG Exposures per NACE Paper No. 04109²

OCTG	Stress	Temp.	Duration	Solution	Initial pH	pH ₂ S	Purge Gas
C110	80% SMYS	73°F 23°C	720 hrs	5 wt% NaCl 4 g/L Sodium Acetate	3.7	0.0275 bara (0.40 psia)	2.75% H ₂ S Balance CO ₂
C110	80% SMYS	73°F 23°C	720 hrs	5 wt% NaCl 4 g/L Sodium Acetate	3.7	0.175 bara (2.54 psia)	17.5% H ₂ S Balance CO ₂
C110	80% SMYS	73°F 23°C	720 hrs	5 wt% NaCl 4 g/L Sodium Acetate	3.7	0.35 bara (5.08 psia)	35% H ₂ S Balance CO ₂

Table 2
Test Matrix for C110 FFP OCTG Exposures per NACE Paper No. 05086³

OCTG	Test Type	Temp.	Duration	Solution	Initial pH	pH ₂ S	Purge Gas
C110	Tensile at 94% AYS	24°C (75°F)	720 hrs	5 wt% NaCl	3.7	0.07 bara (1 psia)	7% H ₂ S Balance CO ₂
C110	DCB	24°C (75°F)	720 hrs	5 wt% NaCl	3.7	0.07 bara (1 psia)	7% H ₂ S Balance CO ₂
C110	DCB	24°C (75°F)	720 hrs	5 wt% NaCl	3.7	0.21 bara (3 psia)	21% H ₂ S Balance CO ₂
C110	DCB	4°C (40°F)	720 hrs	5 wt% NaCl	3.7	0.21 bara (3 psia)	21% H ₂ S Balance CO ₂
C110	DCB	43°C (110°F)	720 hrs	5 wt% NaCl	3.7	0.21 bara (3 psia)	21% H ₂ S Balance CO ₂

OVERVIEW AND COMMENTS ON OCTG SSC-RELATED STANDARDS

The practice of SSC testing has been modified slightly over time through the revision of standards and the introduction of new, more widely-recognized standards. For OCTG SSC, four of the most relevant standards are EFC 16, NACE MR0175 / ISO15156-2, NACE TM0177, and API 5CT^{1,4-6}. EFC 16 is generally seen as providing the original instructions for testing in FFP sour conditions which were adopted with slight alterations into NACE MR0175 / ISO15156-2. TM0177 is referenced by both EFC 16 and NACE MR0175 / ISO15156-2 and has limited explicit instructions on FFP sour testing with the focus being primarily on full sour tests and tests in support of API 5CT.

EFC 16 defines the FFP test solution as 50 g/L NaCl with 4 g/L sodium acetate with the pH adjusted by addition of HCl or NaOH to the target value⁴. The document calls for control of the pH by periodically regenerating the solution through adjustment of the pH to avoid any change greater than 0.1 pH units. It also notes that for conditions “requiring a less stringent environment to represent lower concentrations of H₂S, the solution can be saturated with a gas containing a mixture of H₂S and CO₂...”⁴.

NACE MR0175 / ISO15156-2 adopted the EFC 16 approach to FFP testing with some minor modifications for more allowances in testing approach. FFP testing requirements are defined in Table B.1 in the document where 5 wt% NaCl and 0.4 wt% sodium acetate with adjustment of the pH using HCl or NaOH paired with an H₂S partial pressure is the defined environment⁵. The pH control is not explicitly mandatory, with the footnote stating “For SSC tests with pH control, the pH value during tests should be less than or equal to the required value. Control to within a range of 0.1 pH units is achievable in practice”⁵. The balance gas to the H₂S is also not defined.

The current version of TM0177, TM0177-2016, does not explicitly address FFP testing environments for carbon and low alloy steels with three options existing⁶:

1. Solution A – 5 wt% NaCl, 0.5 wt% acetic acid solution saturated with >99.5% H₂S
2. Solution B – 5 wt% NaCl, 2.5 wt% acetic acid, 0.41 wt% sodium acetate solution saturated with >99.5% H₂S
3. Solution D – 5 wt% NaCl, 0.4 wt% sodium acetate solution, pH adjusted by HCl to 3.8 to 4.0 solution saturated with 7.0 +/- 0.3% H₂S / balance N₂ mixed gas. The final pH shall not exceed 4.6. This specific environment is defined to support API 5CT SR 39¹.

To address the lack of FFP options in TM0177-2016, current proposed edits to the document would permit either H₂S / CO₂ or H₂S / N₂ mixed gases to be used with any of the solutions and Solution D to be adjustable to FFP pH values.

CURRENT PRACTICE AND MOTIVATION FOR EXPERIMENTAL WORK

The review of the different approaches and requirements in the OCTG SSC-related standards led the authors to question how the requirements impact the technical validity and ultimate conservatism in using pass/fail and sour fracture toughness results in OCTG deployment in well construction and completion.

The current practice within Shell for low alloy steel OCTG qualifications is to rely on historical data available in a statistical model or to conduct new FFP testing as required. The statistical model is constructed of >1,000 datapoints for K_{ISSC} of low alloy steel OCTG generally resulting from tests in three (3) general classes:

1. TM0177 Solution A or Solution B with >99.5% H₂S
2. Solution D as defined in TM0177 or modified with different concentrations of H₂S/N₂
3. Solution B or modified Solution B at different pH levels with different concentrations of H₂S/N₂ mixed gas

Using this dataset, the statistical model identified several critical parameters defining K_{ISSC} , with final pH, rather than initial pH, being one of the most influential parameters. The findings of the model have therefore driven the use of stronger buffer solutions to conduct FFP tests in recent years. On reflection of recent publications showing compelling evidence that K_{ISSC} values may be lower in strong acetate buffers, such as Solution B, compared to weaker buffers, the authors reviewed the new publications and internal data and concluded that there may be more to the control of sour fracture toughness beyond simply the final pH value⁷. This led to the motivation to directly compare material response to sour exposures in strong acetate buffered solutions with weakly-buffered solutions with the same final pH values.

In addition to the buffer chemistry, given the basis of the model, the requirements of the testing standards have led to the question if using N₂ balance gas is invalid or improper for FFP testing. There have been suggestions to normalize the use of CO₂ balance gas in NACE sour testing requirements for FFP conditions which have not been incorporated but have generated discussion. In the opinion of the authors, the N₂ balance gas in place of CO₂ balance gas should provide either an equivalent or more conservative, i.e. lower sour fracture resistance, result. This opinion stems from the driver of the corrosion being the hydronium ions (pH) present which suggests that experiments under equivalent pH should result in similar corrosion rates. In order to support this opinion, a direct comparison of the two balance gases under otherwise identical conditions using a well-controlled experiment was desired.

EXPERIMENTAL PROCEDURE

Two different grades of OCTG of varying strength, chemistry, and quality were subjected to sour exposure tests. The tests set out to compare multiple parameters – buffer chemistry, final pH, N₂ vs. CO₂ balance gas – on the corrosion and sour cracking performance of the two OCTG grades. Tests consisted of continuously replenished tank exposures and fixed inventory solution in tanks under continuous mixed gas purge. Multiple specimen types were exposed for various purposes:

1. Rectangular coupons for assessment of weight-loss corrosion and scale analysis
2. Four-point bent beam (FPBB) specimens for assessment of sour crack initiation
3. Double Cantilever Beam (DCB) specimens for assessment of sour crack propagation / fracture toughness

Materials

Grades of OCTG, C110 and P110 were prepared into the different specimen types used in sour exposure testing. The chemistry and mechanical properties of the two grades are presented in Table 3 and Table 4 for reference.

Table 3
Nominal Chemical Composition (wt%) and Mechanical Properties of C110 Low Alloy Steel

C	Mn	Si	Cr	Mo	P	S	Ni	Fe
0.27	0.30	0.24	0.90	0.80	0.017	0.002	0.05	Bal.
Average HRC: 27		YS: 770 MPa (111.7 ksi)			UTS: 846 MPa (122.7 ksi)			RA: 37%

Table 4
Nominal Chemical Composition (wt%) and Mechanical Properties of P110 Low Alloy Steel

C	Mn	Si	Cr	Mo	P	S	Ni	Fe
0.27	1.13	0.29	0.43	0.06	0.014	0.004	0.06	Bal.
Average HRC: 31		YS: 897 MPa (130.1 ksi)			UTS: 972 MPa (141.0 ksi)		RA: 29%	

Testing Approach and Details

Sour exposure testing of coupons, FPBBs, and DCBs of the OCTG grades was performed in glass tanks for a total duration of 21 days. The longer duration was considered a compromise between the typical 30-day exposure for crack initiation testing and the typical 17-day exposure for DCB specimens to reach crack arrest. All tests were performed at ambient pressure and room temperature with a pre-mixed gas purge and a solution composition corresponding to either NACE TM0177 Solution D or a modified Solution B with an initial pH 4.0 where the total acetate ion content reflected that of Solution B but more sodium acetate was used in place of acetic acid; modified Solution B composition was 5 wt% NaCl, 1.094 wt% sodium acetate, and 2.00 wt% acetic acid. Tests were split into two approaches with half of the tests in liquid-full tanks with pumps continuously replenishing solution at a nominal rate of 5 mL/min. that was equilibrated with the test gas in a separate feed barrel and the other half conducted in a typical NACE test approach with a fixed inventory of solution that is continuously purged.

Details of the test exposures are provided in Table 5. A schematic of the exposure tests is presented in Figure 1.

Table 5
Test Matrix for OCTG Exposures for Corrosion and H₂S-related Cracking

Test ID	Setup	Solution	V:SA ^a (mL/cm ²)	Gas	DCBs ^b	Pre-crack?	FPBB ^c	Coupon
1	Flowing Solution	Solution B Mod. pH 4	12	7% H ₂ S/N ₂	4 C110	Yes	2 P110	3 P110
					4 C110	No	2 C110	3 C110
2	Flowing Solution	Solution D pH 4	12	7% H ₂ S/N ₂	4 C110	Yes	2 P110	3 P110
					4 C110	No	2 C110	3 C110
3	Flowing Solution	Solution D pH 4	17	7% H ₂ S/CO ₂	4 C110	No	2 P110	3 P110
							2 C110	3 C110
							2 P110 ^d	
4	Purge Gas	Solution B Mod. pH 4	17	7% H ₂ S/N ₂	4 C110	No	2 P110	3 P110
							2 P110 ^d	3 C110
5	Purge Gas	Solution D pH 4	19	7% H ₂ S/N ₂	4 C110	No	2 P110	3 P110
								3 C110
6	Purge Gas	Solution D pH 4	19	7% H ₂ S/CO ₂	4 C110	No	2 P110	3 P110
								3 C110

^a V:SA – volume-to-specimen surface area ratio; defined as a minimum of 10 mL/cm² for DCB specimens and 20 mL/cm² for other cracking specimens per TM0177⁶

^b DCBs aimed for wedge displacement of 30 mils.

^c FPBBs stressed to 90% AYS unless otherwise stated.

^d Stressed to 60% AYS.