

Paper No.
16579



The Effect of Mill Scale on OCTG Sour Cracking Resistance

Brian Chambers
Shell Global Solutions US, Inc.
150 N. Dairy Ashford Rd.
Houston, TX 77079
United States of America

Manuel Gonzalez
Shell Global Solutions US, Inc.
150 N. Dairy Ashford Rd.
Houston, TX 77079
United States of America

Xin Long
Shell International Exploration and Production
150 N. Dairy Ashford Rd.
Houston, TX 77079
United States of America

ABSTRACT

There exists a commonly-held belief that as-delivered oil country tubular goods (OCTG) possess superior resistance to sulfide stress cracking (SSC) than standardized testing for SSC may identify. This belief relies on the nature of the mill scale present on OCTG being a barrier to corrosion and hydrogen permeation that would act to retard SSC. Despite the popularity of this belief, limited data assessing this hypothesis exists in the public domain.

A laboratory study was conducted to assess both the corrosion behavior and hydrogen permeation through API⁽¹⁾ C110 material in two conditions: 1) mill scale removed with typical NACE⁽²⁾ TM0177 surface finish; and 2) mill scale intact. The study was performed on samples with and without applied stress in NACE TM0177 Solution B with 7% H₂S/N₂ gas purge. The findings indicated that samples with mill scale intact exhibited both higher corrosion rates and higher hydrogen flux in the conditions assessed. Based on the results of the study, it was hypothesized that the higher surface roughness on as-received material contributes to the higher apparent corrosion rate and hydrogen permeation. Per the outcome of this work, reliance on mill scale for either corrosion or cracking protection is considered ill-advised.

Key words: H₂S, sour, sulfide stress cracking, mill scale, OCTG, hydrogen permeation

⁽¹⁾ American Petroleum Institute (API), 1220 L St., N.W., Washington, DC 20005-4070.

⁽²⁾ NACE International, 15835 Park Ten Place, Houston, TX 77084, USA.

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 materials, the dominant EAC concern is sulfide stress cracking (SSC), caused by hydrogen embrittlement in low pH H₂S-containing aqueous conditions in the well. Well materials are typically utilized in the as-received condition with mill scale intact on the surfaces of the steel.

Determination of suitability of LAS OCTG materials is typically done using guidance of NACE MR0175/ISO⁽³⁾15156-2, often supplemented by standardized test methods per NACE TM0177 or NACE TM0316¹⁻³. The test methods utilize specimens removed from the wall of the material which has controlled surface finishes and remove any previously present mill scale. The typical rationale for not assessing the mill scale in the SSC testing is that it is both more conservative and more reproducible to expose a fresh metal surface with a controlled surface finish. This rationale extends into a commonly-held belief that the presence of the mill scale in actual products will provide more resistance to SSC by acting as a barrier to corrosion and hydrogen permeation.

Mill scale results from the hot forming or heat treatment processes of steel and consists of mixed iron oxides such as iron (II) oxide (FeO), iron (III) oxide (Fe₂O₃), and magnetite, an iron (II,III) oxide (Fe₃O₄). In aerated seawater exposures, there is evidence that mill scale acts as a cathode compared to the bare steel and may result in increased localized corrosion rates⁴. In sour corrosion experiments, corrosion rates for mill-scaled specimens were observed to be similar to or greater than those for cleaned specimens⁵.

This paper presents the results of a laboratory study conducted to assess the tendency of mill scale to retard SSC through measurements using hydrogen permeation and corrosion in a typical NACE test solution.

EXPERIMENTAL PROCEDURE

API 5CT compliant C110 grade OCTG material was assessed in two preparation conditions⁶:

1. Mill scale removed with typical TM0177 surface finish, referred to as “without scale” or “polished” herein; and
2. Mill scale intact, referred to as “with scale” or “mill scale intact” herein.

Hydrogen permeation measurements were performed on the material both in the stressed and unstressed state. Other electrochemical measurements assessing the corrosion rate and corrosion potential were also performed on material in the unstressed state. All tests were performed in a strong buffer solution at typical sour conditions relevant for C110 service.

⁽³⁾ International Organization for Standardization ISO Chemin de Blandonnet 8 CP 401 1214 Vernier, Geneva, Switzerland

Testing Approach and Details

C110 OCTG material both with and without mill scale was subjected to electrochemical measurements while exposed to a single exposure environment.

Material

C110 is a Cr-Mo type OCTG with a quenched and tempered martensitic microstructure; a single C110 material heat was used for all testing reviewed herein.

Table 1
C110 Material Dimensions and Average Mechanical Properties

Outer Diameter In mm (inches)	Wall Thickness In mm (inches)	Actual Yield Strength In MPa (ksi)	Tensile Strength In MPa (ksi)	Elongation %	Transverse Charpy Impact In N-m (ft-lbs)	Average Hardness HRC		
						ID	MW	OD
355.6 (14)	20.6 (0.812)	770.1 (111.7)	846.0 (122.7)	37.3	182.1 (134.3)	25.9	27.1	26.3

Table 2
C110 Nominal Material Composition (%)

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.

Test Specimen Preparation

Unstressed exposure specimens for hydrogen permeation and electrochemical tests were removed from the C110 OCTG material and were nominally 25.4 mm (1 inch) x 25.4 mm (1 inch) x 7.6 mm (0.3 inches) thick. For mill scale intact specimens, the ID surface condition of the OCTG was retained on one side of the specimen and, if used in hydrogen permeation testing, the other polished to 600 grit surface finish. Other specimens, referred to as polished specimens hereafter, were prepared by removing the mill scale and polishing any surface used for experiments to 600 grit. An additional set of specimens for electrochemical measurements were prepared with an intentionally rougher surface where blast media (Black Beauty[†]) was used to remove the mill scale.

Stressed exposure specimens for hydrogen permeation tests were removed from the C110 OCTG at the ID surface and the surface retained for mill scale intact specimens and the 600 grit surface finish applied to other surfaces as noted in the previous paragraph. The specimens were flat tensile type with nominal dimensions of 101.6 mm (4 inches) x 19.1 mm (0.75 inches) x 8.3 mm (0.3 inches) thick gauge section and 38.1 mm (1.5 inches) wide grip area.

The surface roughness of the different steel surface conditions was measured on example coupons from each surface preparation by profilometry and compared; see Table 3. One coupon was measured by profilometry as prepared with mill scale intact and then measured again after polishing to 600 grit; a separate coupon was prepared and blasted in order to create a surface with similar surface roughness as the mill scale.

[†] Trade name.

Table 3
Surface Roughness Measured by Profilometry on Example Coupons with Different Surface Preparation Procedures

Material	ID #	Surface Condition	Standard Deviation of Height	Maximum Height Difference	Average Value of Height Difference
C110	16	Mill Scale Intact	33 μm	257 μm	26 μm
	16	Polished (600 grit)	20 μm	127 μm	16 μm
	17	Blasted	39 μm	278 μm	30 μm

Hydrogen Permeation Testing

Hydrogen permeation tests were performed using a Devanathan cell method per a modified ASTM⁽⁴⁾ G148 methodology with a 1 cm² area of steel exposed on both the charging and oxidation sides of the cell⁷. The hydrogen charging side of the cell was filled with NACE TM0177 Solution B, initial pH 3.5, continuously purged with 7% H₂S / balance N₂ gas during the test. Ten (10) total experiments were performed as detailed in Table 4. Five tests were executed on specimens with the mill scale intact and five on specimens with polished surface finish; of those, only a single test was run in each surface finish condition under load with the remaining tests without applied load. A photograph showing the specimen installed in the cell with the load frame is provided in Figure 1. The purpose of the tests was to compare results to examine the effects of mill scale and stress and, as such, the effect of membrane thickness was not performed; a previous paper reviews the validity of the membrane thicknesses used⁸.

Table 4
Summary of Hydrogen Permeation Experimental Parameters

Material	ID #	Exposed Surface ^a	Stress Level	Environment	Sample Thickness
C110	261	Mill Scale Intact	80% AYS	TM0177 Solution B with 7% H ₂ S/N ₂ Purge Gas	0.829 cm
	262		None		0.812 cm
	281		None		0.736 cm
	284		None		0.730 cm
	286		None		0.737 cm
	264	Polished (600 grit)	80% AYS		0.753 cm
	263		None		0.758 cm
	292		None		0.714 cm
	296		None		0.713 cm
	298		None		0.773 cm

^a Charging side of Devanathan cell. Oxidation side for all specimens was 600 grit polished.

⁽⁴⁾ ASTM International (ASTM), 100 Barr Harbor Dr, West Conshohocken, PA 19428-2959