

Effect of H₂S on the Corrosion and Cracking Behavior of Welded API 5L X65 Steel in Supercritical CO₂

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ABSTRACT

Welded API X65 steel specimens were prepared and these were then tested in de-aerated NaCl solution (1000 mg L⁻¹) for 30 days purged with (i) 10 MPa CO₂ and (ii) a mixture of 9.9 MPa CO₂ and 0.1 MPa H₂S. Tests were conducted at 40 °C with one set of specimens submerged in the solution and the other suspended above it. Two sets of specimens were prepared- (i) for corrosion test with no applied stress, and (ii) for stress corrosion cracking (SCC) test using a four-point method by applying 90% of 0.2% proof stress. For four-point testing, specimens were extracted transverse to the weld and were tested with the weld centred on the loading span with the weld root in tension. After completion of exposure, the specimens' mass increased and microstructural characterization revealed that the specimens formed a scale. The presence of 0.1 MPa H₂S reduces the calculated corrosion rate of carbon steel parent due to preferential formation of sparingly soluble mackinawite. Some fine-scale features were seen only on the tensile surface of the stressed steel specimens. These fine-scale features were deeper (length>cross-section) in specimens tested in the vapour phase. These features, however, will not be visible when seen under light optical microscope (10 x) by visual examination only.

Key words: welded pipe, sour corrosion, cracking, SSC, supercritical CO₂

INTRODUCTION

In the O&G sector, carbon steels such as API 5L X65 is widely used due to its high strength and low cost. However, these steels tend to corrode in the presence of wet CO₂, particularly in the presence of dissolved salts and acids.¹⁻⁵ Other metals, alloys and polymers also degrade in the presence of high pressure gaseous and supercritical CO₂.⁶⁻¹² The corrosion rate of carbon steels in some aqueous environments have been reported to be more than a few millimeters per year.⁹⁻¹⁰ Such high corrosion rates are unacceptable. Further, in situations where wet H₂S is present cracking can be an issue for high strength steels. If the corrosion rate is too high in such environments, use of costly corrosion resistant alloys (CRAs) is recommended.¹ However, the cost of such materials often prohibit their wider adoption. There are several publications elucidating the effect of steels in H₂S/CO₂, however, the behaviour of welded steel has not been explored in detail, particularly in supercritical CO₂. This paper

addresses the above knowledge gap and explores the behaviour of welded steel in supercritical CO₂ containing H₂S.

EXPERIMENTAL PROCEDURE

Sample preparation

Specimens were cut from either TIG welded pipes or plates, as shown in Figure 1, with approximate dimensions of 30 × 30 × 5 mm. Specimens were ground and polished to 1200 grit finish, and washed with acetone. The surface containing the weld was washed with acetone in an ultrasonic bath for about 3-5 minutes to remove grease. Holes were drilled in the specimens prior to any grinding and cleaning operation, to attach them to the specimen support arrangement (Christmas tree) while testing.

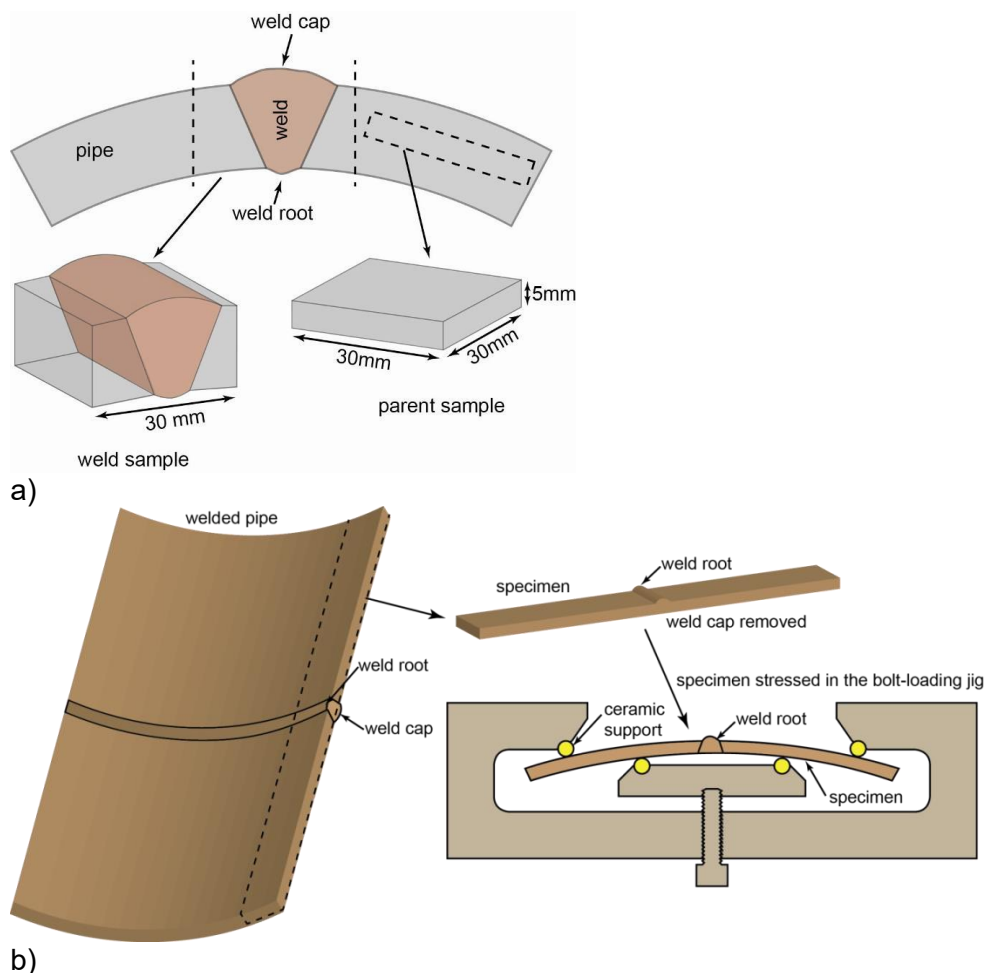


Figure 1: Schematic of the location from which the weld and parent specimens were taken for corrosion testing (a) and stress corrosion cracking tests (b). The dimensions shown are not to scale.

Testing and Characterization of specimens

Corrosion and cracking tests

The specimens were photographed before testing (Figure 2). One specimen of each type was placed in autoclaves and de-aerated chloride solution (1000 mg L⁻¹) was introduced and then heated to 40 °C. Subsequently, the pressure was raised to the test pressure 10 MPa by pumping CO₂ or a mixture of CO₂ and H₂S. The tests ran for 30 days.

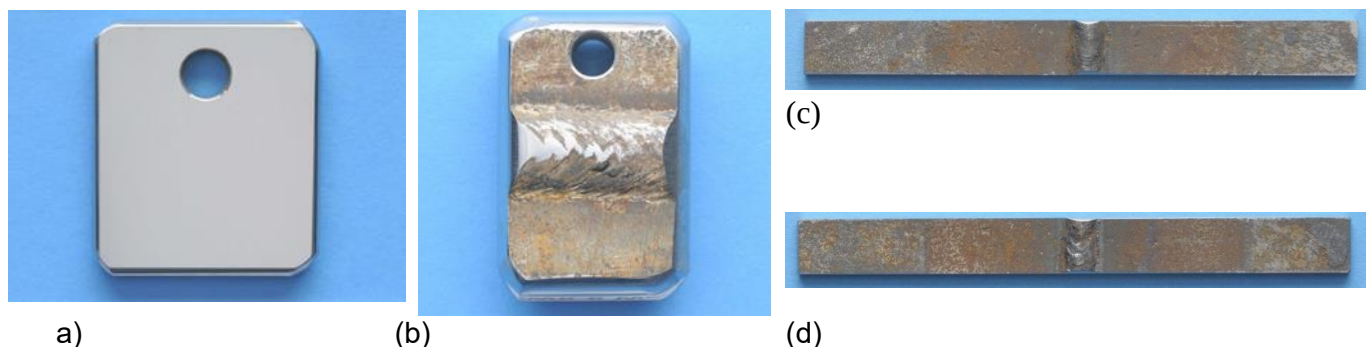


Figure 2: Photographs of some of the specimens: parent (a), weld (b), and SCC specimens with weld (c, d) before testing.

Duplicate four-point bend test specimens (with dimensions of 100 x 10 x 3 mm) for testing under stress using constant deflection (bolt-loading) were prepared for cross-weld tests. Specimens were extracted transverse to the weld and were tested with the weld centred on the loading span with the weld root in tension, as shown in Figure 1b. Strain gauges were attached and the welds were loaded to 90% of 0.2% of proof stress. In all cases half of the specimens were submerged in the test solution and the rest were suspended above it. The experimental test matrix is shown in Table 1.

Table 1: Experimental test matrix

Material	Test Number	Test condition					
		Temp. (°C)	Nominal CO ₂ pressure, (MPa)	Nominal H ₂ S pressure, (MPa)	Cl ⁻ , (mg L ⁻¹)	Specimens suspended in the vapor space	Specimens submerged in aqueous phase
API 5L X65: Parent and Weld	A	40	10	0	1000	A1	A2
						A3	A4
	B	40	9.9	0.1	1000	B1	B2
						B3	B4

Characterization of specimens

Specimens (both parent and weld) tested in different environments were analyzed. If a thick scale was observed, x-ray diffraction was carried out on the flat surface of the parent sample to gather information regarding the phases present. One set of specimens was sectioned, cold mounted and polished prior to metallographic examination. The thickness of the scales formed on parent and weld specimens was determined from the metallographic studies.

To determine the corrosion rate, the procedure detailed in ASTM G1 was followed. The specimens were initially cleaned and weighed before exposure testing, and subsequently assessed upon completion of the test. This procedure involves cleaning the specimens to remove the corrosion products and measuring the mass change relative to initial mass before exposure. To remove corrosion scales an inhibited cleaning solution was used comprising 20 g Sb₂O₃ and 50 g SnCl₂ in 1000 ml HCl, (also called Clarke's reagent). Clarke's reagent poured in a beaker placed in an ultrasonic bath and the specimens were immersed in it for two minutes at room temperature. This cleaning procedure was repeated several times for complete removal of the corrosion products.

The average corrosion rate (in mm/y) was determined by using the equation below:

$$\text{Corrosion rate} = \frac{8.76 \times 10^4 \times w}{A \times t \times \rho} \quad (1)$$