

MIC Impact on Mechanical Property Degradation of X80 Pipeline Steel by A Sulfate Reducing Bacterium

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ABSTRACT

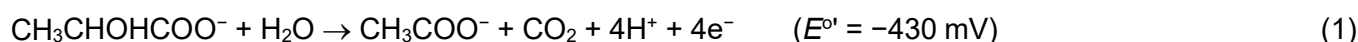
Apart from pinhole leaks, MIC (microbiologically influenced corrosion) can also cause catastrophic failures such as pipe rupture and support beam collapse due to mechanical strength degradation or stress corrosion cracking. In this work, X80 pipeline steel dogbone coupons and square coupon were immersed in 150 mL *Desulfovibrio vulgaris* (a sulfate reducing bacterium or SRB) broths for up to 14 days. The headspace volumes in the anaerobic bottles were varied from 150 mL to 300 mL to increase MIC severity. After 14 days of incubation at 37°C, the sessile cell counts were 6.5×10^7 cells/cm² for 150 mL, 2.3×10^8 cells/cm² for 200 mL and 1.4×10^9 cells/cm² for 300 mL headspace volumes, respectively owing to reduced H₂S toxicity in the broth with a larger headspace. Weight losses were 1.7 mg/cm², 1.9 mg/cm² and 2.3 mg/cm² for 150 mL, 200 mL 300 mL headspace volumes, respectively. The corresponding pit depths were 2.6 μm, 4.2 μm and 6.2 μm for 150 mL, 200 mL and 300 mL headspace volumes, respectively. Electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR) and potentiodynamic polarization results corroborated the increasing weight loss and pitting data trends. Tensile testing after the 14-day immersion indicated that more severe MIC pitting led to a higher ultimate strain loss by up to 22%, while the ultimate strength losses for all headspace volumes were quite small (5% and below).

Key words: MIC, mechanical property, sulfate reducing bacteria, tensile test, H₂S.

INTRODUCTION

MIC has become a major concern in marine, oil and gas, and water utilities industries, etc. MIC accounts for 20% of all of corrosion losses.¹ Walsh estimated that MIC leads to substantial financial losses of approximately \$30-50 billion per year in the US.² In addition to pinhole leaks, MIC can cause mechanical property degradation, leading to metal fracturing/rupturing and cracking that reduce equipment service lifespan.³ Most MIC studies so far focused on pitting corrosion. There is a lack of studies on the impacts of MIC on mechanical property degradation. In practical applications, disastrous consequences such as pipeline rupture and support beam collapse can be caused by mechanical property degradation due to MIC.

SRB are a major type of microbes that cause MIC. SRB can acquire energy by oxidizing organic substances or H_2 while reducing sulfate (SO_4^{2-}) to hydrogen sulfide (H_2S) and other sulfide species.⁴ When sulfate acts as the electron acceptor and lactate (soluble) as the electron donor for SRB respiration, the redox reaction occurs entirely in the SRB cytoplasm to generate energy.⁵



In these two reactions, E° is the reduction potential (vs. SHE) at 25 °C, pH 7, and 1 M solutes (or 1 bar gases). SRB sessile cells require energy to maintain themselves. When there is a lack of carbon source in the local environment near the bottom of an SRB biofilm, elemental iron can provide the electrons for SRB survival, which leads to MIC. E° of Fe^{2+}/Fe is similar to that of acetate + CO_2 /lactate.⁶ This means elemental Fe is as energetic as lactate for SRB.



Therefore, the cell potential (ΔE°) of the redox reaction combining Reactions (3) and (2) above is +230 mV, which results in a negative Gibbs free energy change, indicating that the overall corrosion reaction is thermodynamically favored.⁷ Electrons from extracellular iron (insoluble) oxidation must be transported across the SRB cell wall to the SRB cytoplasm for sulfate reduction. This kind of electron transfer process is known as extracellular electron transfer (EET), an important topic in microbial metabolism for energy production.⁴ *D. vulgaris* MIC of carbon steel observes the EET-MIC theory according to the evidence provided by carbon source starvation tests and electron mediator tests in the literature^{5, 8, 9}. Experimental data have rather conclusively shown that H_2S is not the cause of *D. vulgaris* (a typical SRB strain) corrosion of carbon steel at near neutral broth pH.⁹ Typical SRB MIC tests are not like abiotic H_2S corrosion which involves acidic pH.

X80 carbon steel is widely used in many industries because of their low cost and ease of fabrication. However, X80 steel pipelines may suffer from both MIC and mechanical property degradation caused by MIC. This study investigated the effects of SRB on MIC and the subsequent mechanical property degradation of X80 pipeline steel.

In the past, most investigations focused on MIC pitting only. Not many studies paid attention to the MIC effects on the degradation of mechanical properties. MIC pitting of metal surfaces weaken the metals.⁹⁻¹⁴ Pit density and depth both impacted the mechanical properties of materials such as elongation.¹⁵ In abiotic corrosion studies, Saad-Eldeen et al. found that corrosion activity degraded the ultimate strength of steel.¹⁶ It is suggested that when SRB are present, some engineering materials are likely to fail in a relatively shorter time than in an abiotic environment.¹⁷ One study showed that the ultimate strength and ultimate strain were reduced significantly in the presence of the *Pseudomonas* species due to the biofilm formation and the resultant MIC process.¹⁸ In another study, the presence of corrosive *Bacillus megaterium* bacterium adversely decreased the mechanical parameters such as yield stress, ultimate strength and elongation of an Al-Cu alloy.¹⁹

It has been known that in carbon steel MIC by SRB, a larger headspace allows more H_2S to escape from

the broth. This reduces the H₂S toxicity in the broth, allowing better planktonic and sessile SRB growth, and thus leading to more severe MIC.¹² In this study, dogbone coupons made of X80 carbon steel were used to investigate mechanical property degradation as a consequence of exposure to varied severity of MIC pitting by SRB, which was achieved by varying the headspace. After SRB exposure in anaerobic bottles, X80 dogbones were analyzed for MIC pitting and then tested on a tensile machine to measure mechanical property damages. Square X80 coupons were used to obtain weight loss. Square X80 coupons were also used as working electrodes in electrochemical glass cells to measure MIC severity electrochemically to corroborate weight loss and pit depth data trends from anaerobic bottles and to provide transient corrosion behavior.

EXPERIMENTAL PROCEDURE

X80 steel composition is listed in Table 1. Dogbone coupons were too heavy to measure milligram weight loss accurately. Thus, three square coupons, each with a 1 cm² unpainted top surface (all other surfaces were covered with a polytetrafluoroethylene paint), were incubated in each anaerobic bottle to obtain one MIC weight loss data point. Square coupons (1 cm² exposed surface) were also used as working electrodes in electrochemical glass cells. Dogbone specimens are widely used to test the mechanical property of metal materials.²⁰ The dimensions of the dogbone coupons (Figure 1b) were based on the ASTM E08-04 standard. The dogbone coupons were polished to 1200 grit by the supplier. Each dogbone coupon was painted with Teflon, except for a middle section with a width of 6 mm and length of 22 mm which was exposed upward to the broth. The surfaces of all the square coupons (including the abiotic control and electrode coupons) were sequentially polished with 180, 400 and 600 grit abrasive papers. After that, all the coupons were cleaned with pure isopropanol and dried under UV light for 20 minutes.

Table 1
Composition of X80 steel

Element	C	Mn	Ni	Cu	Si	Mo	Cr	Nb	Ti	Fe
Amount (wt%)	0.050	1.850	0.285	0.246	0.228	0.307	0.016	0.065	0.013	balance

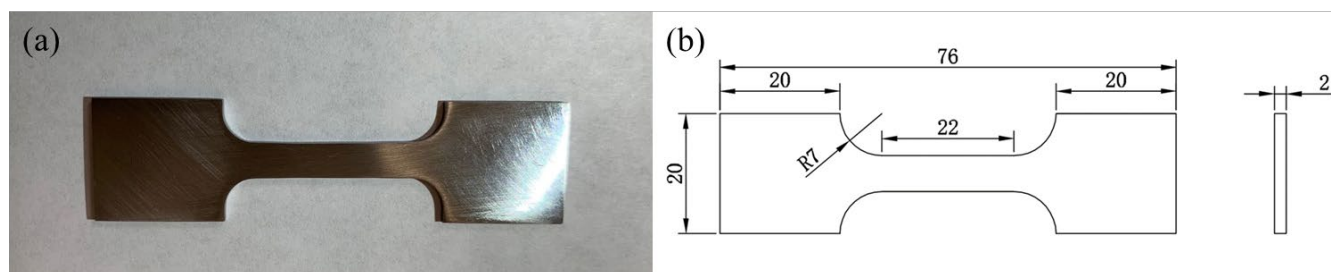


Figure 1. (a) dogbone coupon of X80 steel, and (b) coupon dimensions in mm.²¹

D. vulgaris (ATCC[†] 7757 strain), a common SRB strain in MIC research, was selected for this research. The culture medium was ATCC[†] 1249 medium, which is a modified Baar's medium for sulfate reducers. The culture medium pH was adjusted to pH 7 using a NaOH solution. Dogbone coupons were immersed in anaerobic bottles with 150 mL culture medium and varied headspace volumes (150 mL, 200 mL and 300 mL). The headspace variation was achieved using different bottle sizes and inert glass beads as filler to reduce the available volume. The anaerobic bottles with culture medium were sterilized in an autoclave at 121 °C for 40 minutes. After autoclaving, the SRB culture medium was deoxygenated using filter-sterilized N₂ sparging for more than 45 minutes. One hundred ppm (final) L-cysteine was then added to the culture medium as an oxygen scavenger to reduce dissolved oxygen further and to mitigate any possible oxygen leakage. Each bottle was inoculated with 2 mL SRB seed culture. The abiotic control dogbone coupon was immersed in an anaerobic bottle with 150 ml culture medium and 150 mL headspace without SRB inoculation. Each bottle contained one dogbone coupon. For the weight loss measurement, each bottle contained 3 square coupons.

The concentration of H₂S in the headspace and total pressure in each anaerobic bottle were measured

using a portable H₂S sensor (Model GAXT-H-DL, BW Technologies, Calgary, Alberta, Canada), a digital manometer (Model Xplorer GLX - PS-2002, PASCO scientific, Roseville, CA, USA), respectively. The H₂S sensor has an upper limit of 100 ppm (v/v). If a headspace sample had a higher concentration, dilution was required.⁹

After 14 days of incubation, the X80 square coupons and dogbone coupons were retrieved. The biofilms and corrosion products on the coupon surfaces were removed using a fresh Clarke's solution according to ASTM G1-03 before weighing. After the removal, the maximum pit depth for each dogbone coupon was obtained under an infinite focus microscopy (IFM) machine (Model ALC13, Alicona Imaging GmbH, Graz, Austria). After the pit depth analysis, tensile tests were performed on an electromechanical universal testing machine (E44.304, MTS system, MN, USA) on the same dogbone coupons. The square coupons were cleaned with the Clarke's solution before weighing.

A potentiostat (Model VersaSTAT 3, Princeton Applied Research, Oak Ridge, TN, USA) was used to measure the electrochemical responses of the X80 working electrode (1 cm²) in SRB broth. Each glass cell contained 150 mL deoxygenated culture medium (fixed) with either 150 mL, 200 mL or 300 mL headspace (adjusted using inert glass beads). Each glass cell was inoculated with 2 mL SRB seed culture before incubation at 37°C. A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum plate (10 mm × 10 mm × 1 mm) was used as the counter electrode. The abiotic control working electrode was immersed in an anaerobic bottle with 150 mL culture medium and 150 mL headspace without SRB inoculation. There was no need to vary the headspace for the abiotic control because H₂S escape to the headspace would not occur abiotically. Open circuit potential (OCP), LPR, EIS and potentiodynamic polarization analyses were performed. LPR was scanned at a rate of 0.1667 mV/s in the range of -10 mV to +10 mV vs. OCP. EIS was performed at OCP by applying a sinusoidal voltage signal of 10 mV (amplitude) in the frequency ranging from 10⁴ to 10⁻² Hz. Potentiodynamic polarization curves were measured at the end of the 14-day incubation from OCP to OCP - 200 mV using one working electrode and from OCP to OCP + 200 mV using another working electrode in a different glass cell at a rate of 0.1667 mV/s. The corrosion potential (E_{corr}), corrosion current density (i_{corr}), and anodic and cathodic Tafel slopes (β_a and β_c) were determined from a Tafel analysis of the polarization curves.

RESULTS AND DISCUSSION

Table 2 shows that the H₂S concentrations in the headspace gas phase for the anaerobic bottles (each containing one dogbone coupon) with headspace volumes of 150 mL, 200 mL and 300 mL were 8.50 × 10³ ppm (v/v), 7.75 × 10³ ppm, and 7.28 × 10³ ppm, respectively after the 14-day incubation. The corresponding H₂S concentration in the liquid phase was estimated based on H₂S equilibrium at 37°C according to Ning et al.²² The dissolved [H₂S] in the culture medium in the anaerobic bottles with headspace volumes of 150 mL, 200 mL and 300 mL were 1.06 mM, 0.95 mM and 0.84 mM, respectively (Figure 2 and Table 2). As expected, a larger headspace allowed more H₂S (Table 2) to escape from the liquid phase in order to reach a different H₂S equilibrium between the gas and liquid phases. Figure 2 also shows that the final broth pH values were 7.08, 7.26, and 7.54 corresponding to headspace volumes of 150 mL, 200 mL and 300 mL, respectively. pH increased with the increasing headspace volume, because a larger headspace allowed more H₂S to escape and this takes away more protons from the broth as shown in Reaction (4).¹² According to the literature,¹² a *D. vulgaris* broth in an anaerobic vial usually has near neutral pH because its normal metabolism does not change the scalar or vectorial proton concentration.

