

Effect of Salt Concentration on Uniform Hydrogen Sulfide Corrosion Rate of Pipeline Steel

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ABSTRACT

Large amounts of water can be produced during the production of hydrocarbons from underground reservoirs. Salts are always dissolved in these produced waters. The concentration of dissolved salts can be as high as 400 g/l. For the first time, the effect of salt concentration on uniform hydrogen sulfide (H_2S) corrosion of carbon steel in aqueous solutions is studied. Linear polarization resistance (LPR) and potentiodynamic polarization (PD) experiments were conducted in aqueous solutions at 20°C and pH 5.00 saturated with an H_2S/N_2 gas mixture with a total pressure of 1 bar and H_2S concentration of 100 ppm(v). Two NaCl concentrations were tested: 1 and 20 wt.%. A rotating cylinder electrode with a rotational speed of 1000 rpm was used as the specimen. LPR corrosion rates indicated that H_2S corrosion rate decreased with increasing salt concentration. PD results showed that the corrosion process was under mixed control. Increasing salt concentration retarded both the anodic and the cathodic reactions, and thereby, decreased the rate of uniform H_2S corrosion.

Keywords: hydrogen sulfide corrosion, pipeline corrosion, salt concentration, salinity, rotating disk electrode (RDE), produced water

INTRODUCTION

Large amounts of water can be produced during extraction of hydrocarbons from underground reservoirs.¹ It is well understood that produced waters usually contain high amounts of dissolved salts, up to 28 wt.%.² In addition to salts, dissolved corrosive gases (CO_2 and H_2S) are present in produced water, which make the mixture a complex corrosive environment for metallic parts and equipment used throughout the production process.

Internal H_2S corrosion of carbon steel tubulars often occurs in the oil and gas industry, particularly when drilling deeper to search for new oil and gas reservoirs.^{3,4} In contrast to CO_2 corrosion, a limited number of studies exist for H_2S corrosion. And, to the best knowledge of the authors, no study has been done on the effect of salt concentration on uniform H_2S corrosion. It is necessary to understand H_2S corrosion mechanisms in high saline solutions to develop a correct corrosion prediction. For the first time, the effect of salt concentration on uniform H_2S corrosion of carbon steel in aqueous solutions is presented as part of a wider mechanistic study.

This work, as a small part of a larger joint-industrial project (JIP) focused on corrosion mechanisms related to the internal CO₂/H₂S corrosion of pipeline-grade carbon steel, covers the effect of salt concentration on uniform H₂S corrosion in acidic media. The data presented in this article is used in development of a corrosion-rate-prediction model as one of the goals of the JIP.

In this paper, the effect of NaCl concentration on corrosion behavior of X65 carbon steel was investigated by performing electrochemical experiments in aqueous solutions with two NaCl concentrations at 20°C, 1 bar total pressure, pH 5.00, and 100 ppm H₂S concentration in the gas phase.

EXPERIMENTAL PROCEDURE

Two objectives were followed in this study. First and foremost, to study the effect of salt concentration on H₂S corrosion at low H₂S concentrations. Second, to build experience and confidence in safely working with the poisonous H₂S gas for experiments using H₂S gas at a partial pressure of ~1 bar. The experiments in this part of study were done at pH 5.00 to intensify the contribution of the H₂S buffering effect in the H₂S corrosion process. Bulk solution pH was kept constant at pH 5.00 for experiments at all salt concentrations, so that the only parameter changed in the experiments was NaCl concentration. This testing methodology allowed a better understanding of the effect of salt concentration on the H₂S corrosion process.

Setup and apparatus

Experiments were conducted at 20°C, 1 bar total pressure for two NaCl concentrations of 1 and 20 wt.% in a 2-liter glass cell. The temperature of 20°C was chosen identical to that in CO₂ experiments to allow comparing the corrosion rate measurements in H₂S- and CO₂-saturated solutions[†]. The schematic of the experimental apparatus used in this part is shown in Figure 1.

The gas atmosphere exposed to the solution was an H₂S/N₂ mixture with 100 ppm(v) H₂S gas balanced with N₂ gas. 100 ppm(v) H₂S gas concentration is equivalent to 10⁻⁴ bar H₂S_(g). The H₂S and N₂ gases were mixed, and their ratio was adjusted by using a double-column rotameter. The outlet gas mixture from the glass cell was passed through a saturated NaOH solution followed by an activated carbon-containing flask to scrub H₂S gas from the gas mixture. The scrubbed gas was then sent to a combustion chamber with excess air where the remaining H₂S in the gas stream was converted to sulfur dioxide (SO₂). It has been determined that the combustion process is near 100% conversion and no detectable H₂S remains in the effluent gas.

To adjust the solution temperature to 20°C, water was circulated from an industrial chiller through a copper coil around the glass cell to cool down the solution temperature. In combination with the cooling coil and insulation around the cell, a hot plate was used continuously to balance the temperature at 20 ± 0.5°C.

For each experiment, the desired amount of NaCl was mixed with deionized water (conductivity < 1 μS/cm) in the glass cell. Then, the solution was sparged with the H₂S/N₂ gas mixture for at least 3 h, while being stirred by a magnetic stirrer. The 3 h was identified experimentally as the least amount of time needed to drop the concentration of dissolved oxygen in the solution (~ 2 liter) to less than 10 ppb and saturate the solution with the gas mixture. The dissolved oxygen was measured during the experiments with an Orbisphere[‡] 410 oxygen meter connected to the gas outlet to assure that the oxygen level in the solution was less than 10 ppb. The solution pH was frequently monitored from the beginning

[†] The comparison is not the focus of this study.

[‡] Trade name.

to the end of each experiment. The solution was identified saturated with the gas mixture when solution pH stayed stable ($\Delta pH < 0.01$) for at least 15 min. Double-junction pH probes suitable for concentrated brines and resistant to H_2S were used for the pH measurements.

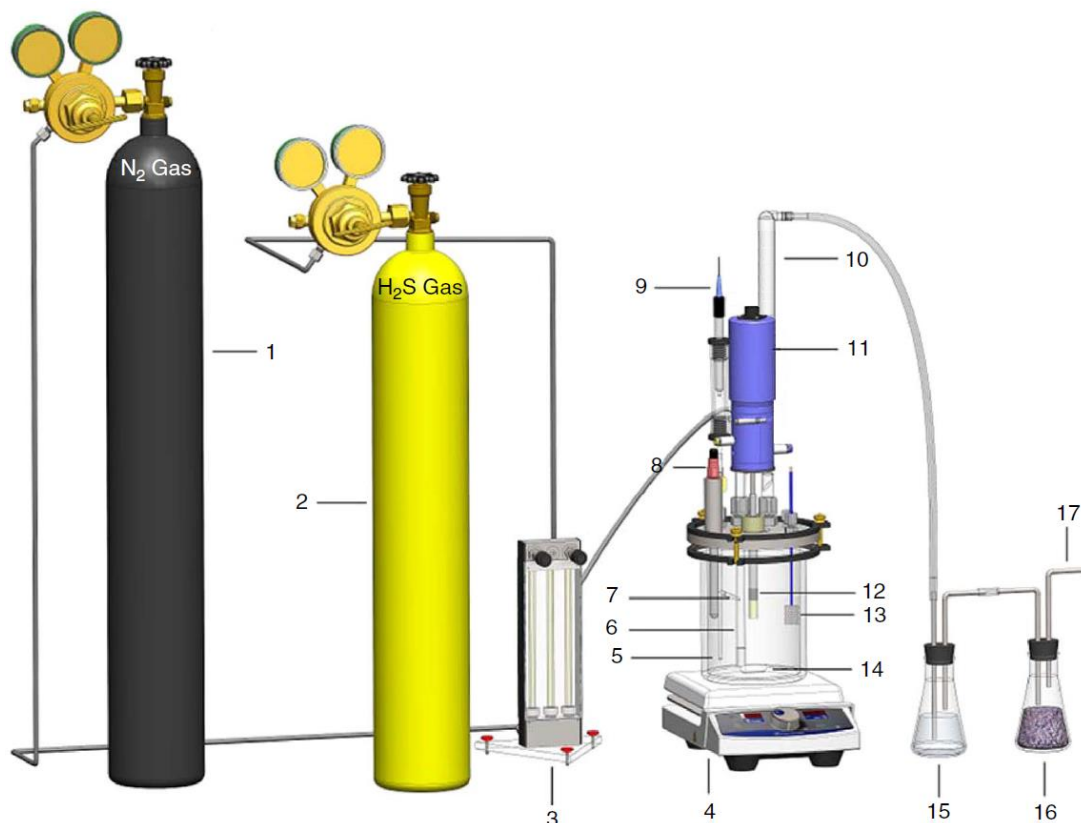


Figure 1. The schematic of the experimental apparatus used for RCE H_2S experiments at pH 5.00 and 100 ppm $H_2S(g)$. The assigned numbers represent: (1) N_2 gas cylinder, (2) H_2S gas cylinder, (3) double-column rotameter, (4) hot plate, (5) thermocouple, (6) gas inlet, (7) Luggin capillary, (8) pH-electrode, (9) reference electrode, (10) gas outlet from the cell, (11) motor, (12) rotating cylinder electrode, (13) platinum coated counter electrode, (14) stir bar, (15) sodium hydroxide solution, (16) activated carbon scrubber, (17) gas outlet to the combustion chamber.

Once a stable pH was attained, the solution pH was adjusted to pH 5.00 by injecting deaerated HCl 0.01 M to the solution. To make sure that solution pH stayed fixed at 5.00, the solution was sparged with the gas mixture for another 0.5 h prior to inserting the specimen into the solution and before beginning the electrochemical measurements. The magnetic stirrer was stopped throughout the electrochemical measurements.

Material tested

The specimen material was API 5L X65 pipeline grade carbon steel.⁵ The chemical composition of this X65 steel is defined in Table 1. The carbon steel microstructure (not shown here) is a uniform, fine structure of pearlite in a ferrite matrix. The RCE specimen used have an outer diameter of 12 mm, a length of 14 mm, and an outer surface area of 5.4 cm^2 . The cell volume to specimen surface area ratio in the experiments was approximately 370 cm^3/cm^2 , which was much larger than the average minimum ratio of 30 cm^3/cm^2 suggested by ASTM G31.⁶ Prior to each experiment, the specimen was sequentially wet polished with 80-, 240-, 400- and 600-grit abrasive papers. Then, the specimen was ultrasonically cleaned in an isopropanol bath for 3 min and dried in a cool N_2 gas stream. The RCE specimen was carefully mounted onto the RCE shaft without touching its surface and the whole assembly was

transferred into the glass cell. The RCE assembly was rotated at 1000 rpm, which simulates the mass transfer conditions in a 10 cm ID pipe with an average flow velocity of 1 m/s.⁷

Table 1. Chemical composition of the experimental carbon steel (API 5L X65) (in wt.%).

Al	As	C	Co	Cr	Cu	Mn	Mo	Nb	Ni
0.028	0.008	0.05	<0.001	0.252	0.173	1.51	0.092	0.034	0.291
P	S	Sb	Si	Sn	Ti	V	Zr	Fe	
0.004	<0.001	<0.001	0.167	0.002	0.012	0.04	<0.001	balance	

Electrochemical measurements

In each experiment, EIS, LPR, and PD sweeps were performed, using the same specimen. First, the EIS was done to measure the solution resistance. Then LPR was conducted for the corrosion rate measurements to identify the overall effect of salt concentration on the H₂S corrosion rate. Finally, PD sweeps were obtained to investigate how individual reaction mechanisms underlying H₂S corrosion are affected by salt concentration. For each NaCl concentration, the experiments were repeated two times.

The LPR technique was performed using a three-electrode setup as shown in Figure 1, using a potential range from -5 mV to +5 mV vs. OCP with a scan rate of 0.125 mV/s. The RCE acted as the working electrode. A saturated Ag/AgCl reference electrode connected to a Luggin capillary served as the reference electrode and a platinized titanium mesh (20 mm × 30 mm) was used as the counter electrode to complete the three-electrode setup. The duration of each LPR measurement was 80 sec. The average Stern-Geary constant (B) for converting the measured polarization resistance into the corrosion rate was determined to be around 18.7 mV/dec. This was done by fitting the PD sweeps via an electrochemical model.⁸ The measured polarization resistance values were corrected for the solution resistance, which was measured by EIS. EIS was done prior to each LPR measurement at OCP with the same electrode setup as for LPR in a frequency range of 10000-0.1 Hz with a peak-to-peak AC voltage amplitude of 10 mV.

For the PD sweep measurements, before starting to sweep the potential, the open circuit potential (OCP) was monitored to ensure having a stable OCP value ($\Delta_{OCP} < 2$ mV/min). The PD sweep experiments were carried out according to the following steps: (1) a cathodic sweep starting from the OCP toward more negative potentials up to -1 V vs. OCP; (2) wait for the OCP to return near its initial value—within a few mV (this took about 1 h); (3) an anodic sweep starting from the OCP to more positive potentials up to 0.35 V vs. OCP. The PD sweep scan rate was 0.125 mV/s. All the PD sweeps were corrected for the solution resistance obtained by EIS. A Gamry potentiostat Reference 600[§] was used for all the electrochemical measurements. Each full set of electrochemical measurements required about 6 h. During each experiment, the increase in the solution pH was less than 0.05 pH units for all NaCl concentrations.

pH measurements

Figure 2 shows the autogenous pH of solution before pH adjustment for the 1 wt.% and 20 wt.% NaCl concentration solutions sparged with an H₂S/N₂ gas mixture at 100 ppm H₂S. The purpose of the dashed line is to just show the trend. The autogenous pH of solution increased with increasing NaCl concentration. The first speculation is that increasing salt concentration decreased H₂S solubility (the

[§] Trade Name

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