

Electrochemical Model of Sour Corrosion of Mild Steel: Validation at High H₂S Partial Pressures

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ABSTRACT

Hydrogen sulfide (H₂S) corrosion of mild steel is a serious concern in the oil and gas industry. However, H₂S corrosion mechanisms, specifically at high partial pressures of H₂S, have not been extensively studied; this is primarily a result of experimental difficulties and associated safety issues. The study reported herein was conducted under well-controlled conditions at H₂S partial pressure of 0.096 MPa, pH values of 3.0 and 4.0, 30°C, and with rotating cylinder speed of 1,000 rpm. Short-term exposures lasting between 1.0 h and 1.5 h were used to avoid formation of any protective iron sulfide layers. The experimental results were compared with a recent mechanistic model of sour corrosion developed by Zheng, et al. (2014). The validity of the model at higher partial pressures of H₂S was challenged as it was uncertain if the mechanisms identified at lower partial pressures of H₂S were still valid. The comparison with the experimental results obtained in the present study indicated a good agreement between the model and the measurements.

KEY WORDS: corrosion rate, hydrogen sulfide, modeling

INTRODUCTION

The focus of the current study is on higher H₂S partial pressures and the corrosion mechanisms of mild steel at those conditions. The key hypothesis is that the

mechanistic model of Zheng, et al.,¹⁻² based on low H₂S pressure data, will successfully work at higher H₂S partial pressures.

Figure 1 shows parity plots where corrosion data from selected open literature high H₂S partial pressure experiments (0.015 MPa H₂S to 1.6 MPa H₂S) are plotted vs. the predictions made by the model. The solid lines in Figure 1 represent a perfect agreement, while the dashed lines represent a factor of two differences between the measured and predicted values. The colors of the symbols indicate data from different experimental conditions and/or studies. The data points are derived from three different high pH₂S corrosion studies, with widely different conditions and with no additional information on underlying corrosion mechanisms. This illustrates that there is a clear lack of reliable, systematically collected, coherent corrosion data from high pH₂S experiments based on sound electrochemical measurements. Therefore, the current study provided a base for validation of mechanisms and models for mild steel corrosion in higher pH₂S environments.

EXPERIMENTAL PROCEDURES

Experiments were conducted in a glass cell, which was filled with 2 L of a 3.0 wt% NaCl aqueous solution. This electrolyte was saturated with H₂S by continuously purging the solution with H₂S gas throughout the experiment. A cylindrical API X65 steel specimen was mounted onto the rotating cylinder electrode (RCE) rotator and inserted into the glass cell for electrochemical measurements. Electrochemical measurements were conducted

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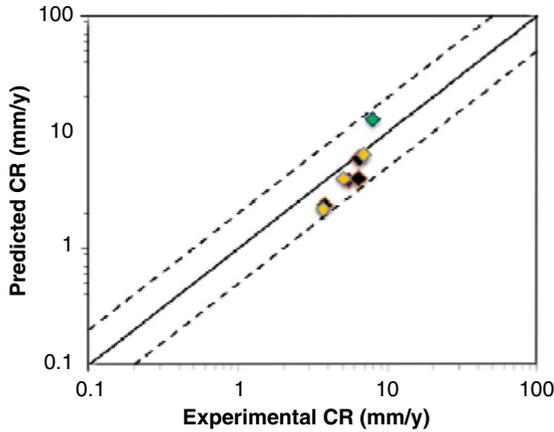


FIGURE 1. Parity plot of the predicted data using Zheng's model when there is no iron sulfide layer vs. experimental data at higher H_2S partial pressures. Kvarekval and Dugstad³ 0.14 MPa H_2S , Abayathna, et al.,⁴ from 0.088 MPa H_2S to 0.015 MPa H_2S , and Liu, et al.,⁵ 1.6 MPa H_2S .

TABLE 1
Experiment Matrix

Parameters	Conditions
Total Pressure	0.1 MPa
Temperature	30°C
Electrolyte	3 wt% NaCl
Test Condition	1,000 rpm
Material	X65
Electrochemical Methods	linear polarization resistance, electrochemical impedance spectroscopy, and potentiodynamic sweeps
p H_2S in the Gas Phase	0 MPa and 0.096 MPa
pH Values	3.0, 4.0, and (± 0.1)

using a three-electrode setup with a mild steel RCE as the working electrode. A platinum mesh plate was used as the counter electrode. An external saturated silver/silver chloride (Ag/AgCl) reference electrode was connected using a KCl salt bridge via a Luggin capillary. The experimental conditions are summarized in Table 1.

RESULTS AND DISCUSSION

To establish a baseline, the model calculations were first compared to potentiodynamic sweep data obtained in N_2 saturated aqueous solutions at pH 3.0. The experimental repeatability and accuracy of the electrochemical measurements were quantified by repeating the experiments multiple times, as shown in Figure 2. Therein, the points represent the average value of the current obtained for different repeats and the error bars denote the maximum and minimum values, all taken at exactly the same potential. Figure 2 shows that there is a very good agreement between

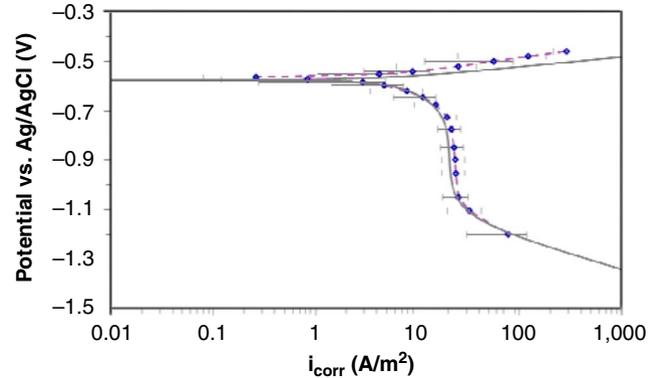


FIGURE 2. Potentiodynamic sweeps on mild steel in N_2 purged solutions, 1 wt% NaCl, 30°C, and 1,000 rpm RCE, scan rate 5 mV/s, pH 3.0 (six repeats).

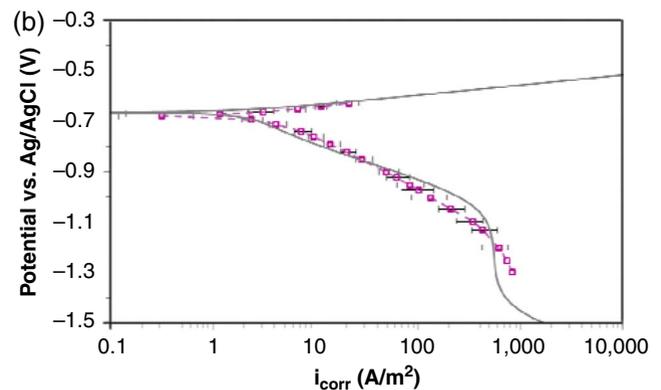
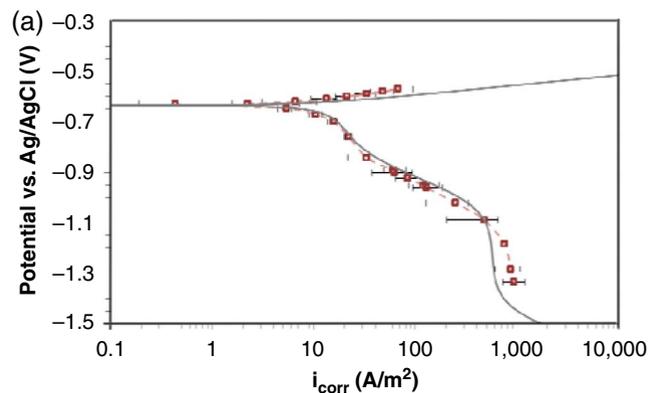


FIGURE 3. Potentiodynamic sweeps on mild steel in H_2S saturated solution with 0.096 MPa H_2S in the gas phase, 3 wt% NaCl, 30°C, and 1,000 rpm RCE, scan rate 5 mV/s, (a) pH 3.0 (five repeats) and (b) pH 4.0 (four repeats).

the model, in solid line, and the measured data, particularly for the cathodic reaction.

In H_2S saturated solution, the effect of pH is shown in Figure 3. In Figure 3(a) the measured data points show an average obtained from five repeats, conducted at pH 3.0. There is a very good agreement between the measured data and the calculated values (solid line), particularly at the lower current densities ($<10 A/m^2$). Similar results were obtained at pH 4.0, see Figure 3(b),

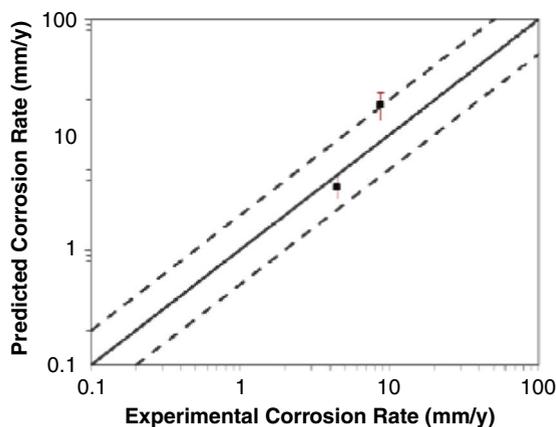


FIGURE 4. Parity plot of the predicted uniform corrosion rate in the absence of an iron sulfide layer on the surface vs. measured linear polarization resistance corrosion rate using a mechanistic sour corrosion model¹ for short-term exposure of mild steel in H₂S saturated electrolyte with 0.096 MPa H₂S in the gas phase, at pH 3.0 and pH 4.0.

which shows the averages of the data collected from four repeated experiments.

To measure the corrosion rate, LPR measurements were conducted in each experiment. The results are presented in the form of a parity plot in Figure 4, which shows a good agreement between the average of the measured and the calculated uniform corrosion rate; a full manuscript on this topic is being prepared for publication.

SUMMARY

❖ The physicochemical processes underlying H₂S corrosion in the absence of protective iron sulfide are similar across a wide range of aqueous H₂S concentrations. It was demonstrated that the mechanistic corrosion model of Zheng, et al.,¹ was successful at extrapolating corrosion rate predictions from low to high pH₂S conditions.

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