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Onset of Corrosion Rate Retardation at Very Low Concentrations of H₂S in a CO₂ Environment

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ABSTRACT

Many experimental studies have indicated that the addition of H₂S on the order of 10⁻¹ mbar to a CO₂ saturated environment can dramatically decrease the corrosion rate at various temperatures. This is likely due to the formation of a very thin layer of iron sulfide (FeS). In this research, the trend in corrosion rate of X65 steel at various H₂S concentrations below 100 ppm (0.1 mbar) in CO₂ at 1 bar total pressure and at various temperatures was studied. Corrosion rate was measured *in situ* using linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS). It was observed that at 30°C, 0.5 ppm H₂S (0.0005 mbar p_{H2S}) had no effect on the corrosion rate compared to that seen in pure CO₂ conditions, whereas 5 ppm H₂S (0.005 mbar p_{H2S}) was able to significantly decrease the corrosion rate. At 80°C, a noticeable decrease was seen at 100 ppm, which was the highest concentration tested. The lack of a decrease in corrosion rate at 0.5 ppm at 30°C is likely due to the low concentration of H₂S molecules available leading to a slowing in the formation of the protective FeS layer. At 80°C, the corrosion rate is significantly higher leading to the necessity of increased H₂S concentrations to form the FeS layer fast enough to see a decrease in the corrosion rate.

Key Words: H₂S Corrosion; Souring

INTRODUCTION

Internal corrosion of mild steel pipelines is a major issue in the oil and gas industry, due to the presence of produced water in the oil and gas being extracted. Oil and gas reservoirs can be divided into two categories: sweet and sour. A sweet reservoir will have the dominant corrosive gas present be carbon dioxide (CO₂), whereas in a sour reservoir the hydrogen sulfide (H₂S) is in a significant enough quantity to have an effect on the corrosion. ISO 15156 states that for sulfide stress cracking, any system with $p_{H_2S} > 3$ mbar was considered to be sour.¹ Several processes can lead to the presence of H₂S in the gas phase. For example, reservoir souring can refer to a situation where H₂S is being generated in a reservoir which was originally sweet or contained no H₂S and was dominated by CO₂. This can occur due to a variety of factors, the most common being biological souring where sulfate reducing bacteria (SRB) are introduced into the reservoir and begin to produce H₂S. It is also possible for the H₂S to already be present in the well, and be activated during the oil and gas extraction. The process of souring often presents as a slow increase in the H₂S content over time.² This means that, in a well which is originally sweet, at the onset of souring the environment in the pipeline will have a large amount of CO₂ with very small concentrations of H₂S present.

There have been studies looking at the trend in corrosion rate with low concentrations of H₂S in a CO₂ environment.^{3,4,5} Previous research into the area of corrosion of mild steel has indicated that the corrosion rate is retarded when low concentrations of H₂S are present in a primarily CO₂ system.^{3,4,5} This retardation in corrosion rate is attributed to the formation of thin layers of iron sulfide (FeS) on the metal surface which slow down the transfer of species to and from the surface. The kinetics of this layer formation process, expressed as scaling tendency (ST), was characterized previously as the ratio of the sulfide layer formation rate (SFR) and the underlying corrosion rate (CR), seen below in Equation 1.^{6,7}

$$ST = \frac{SFR}{CR} \quad (1)$$

This equation is valid when the precipitation and dissolution of the FeS layer play a significant role.⁸ The SFR term refers to the likelihood of a protective layer being formed and is dependent on local conditions near the metal surface, including pH and the presence of both ferrous ions and sulfide species capable of forming FeS. The CR term is the underlying corrosion rate at the metal surface. It can be assumed that the retardation of the corrosion rate in the presence of small concentrations of H₂S can be linked with the value of ST. When the ST has a value greater than 1, this indicates that the formation rate (SFR) is higher than the corrosion rate (CR), so a layer can form which can retard the corrosion rate. If ST has a value lower than 1, the formation rate (SFR) is lower than the corrosion rate (CR), no significant layer formation will be seen, and the corrosion rate will not change.

When the H₂S concentration is gradually increased from zero, in a sweet system, the corrosion rate is expected to eventually reach a minimum value and then begin to increase as the H₂S concentration is increased.^{3,5} It has also been seen that temperature does not greatly affect this phenomenon, and the corrosion rate will be similarly decreased at similar concentrations of H₂S at different temperatures.⁴ However, this previous work failed to go to low enough concentrations to sufficiently establish what trace concentrations of H₂S (<5 ppm) have an effect in the system. These studies⁴ also did not consider other environmental parameters such as pH or fluid velocity and their effect on the system when looking at changes in temperature. The focus of this work is on very low concentrations of H₂S in a CO₂ system to observe which concentrations have no noticeable effect on the corrosion rate. Additionally, a change in the temperature of the experimental system was used to observe its influence on these low concentrations of H₂S that can be present in the system.

EXPERIMENTAL PROCEDURE

A three-electrode glass cell setup, which can be seen below in Figure 1, was used to conduct corrosion experiments at pH 4.0, 1 bar, 30°C and 80°C. The electrolyte used was a 1 wt% NaCl solution. The steel sample used was an X65 steel rotating cylinder electrode (RCE) rotated at 1000 rpm; this was the working electrode. The counter electrode was a platinum covered titanium mesh, with a saturated KCl, Ag/AgCl electrode connected via a Luggin capillary acting as the reference electrode. The reference electrode was maintained at room temperature throughout these experiments using the Luggin capillary. The pH in the system was maintained at 4.0±0.05 for the duration of each experiment. The system was purged with a mixture of CO₂ and H₂S using a system of rotameters to control the flowrates of the gases, and a Gastec[†] pump and detector tubes were used to measure the concentration of H₂S in the gas entering the glass cell. Concentrations tested in this work at 30°C and 80°C are shown below in Table 2. The glass cell was purged for at least one hour prior to introduction of the RCE specimen, which was polished using 600 grit sandpaper until no polishing marks were visible on the sample. Once the sample was inserted into the glass cell, a 1-hour open circuit potential (OCP) measurement was performed to allow the system to stabilize at the corrosion potential. Following this, linear polarization resistance (LPR) measurements were performed every 30 minutes for 4 hours by polarizing the sample from -5 mV to +5 mV from the corrosion potential. Finally, electrochemical impedance spectroscopy (EIS) was performed to determine the solution resistance by scanning a frequency range from 10000 to 0.01 Hz. The corrosion rate was calculated using a *B* value of 26 mV/decade.

[†]Trade name.