

Effect of Trace Concentrations of H₂S Introduced to Existing Sweet Corrosion Product Layers

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ABSTRACT

Simulation of reservoir souring has been a neglected area of corrosion research. The procedure followed herein is to form a sweet corrosion product layer, introduce a low concentration of H₂S in the gas phase (<100ppm) and allow the system to continue to evolve. The experimental apparatus used was a 2L glass cell with an impeller in the center and 5 samples spaced evenly around it to allow for *in situ* corrosion rate monitoring and extraction of specimens for surface analysis. In experiments involving Fe₃C residues the general corrosion rate decreased when H₂S was added to the system. FeS was detected on the samples with the Fe₃C; it is postulated that a thin layer of FeS forms leading to the decrease in general corrosion rate. When the FeCO₃ was challenged with H₂S, the general corrosion rate increased. FeS was detected on the samples, but no significant change was observed in the FeCO₃. However, it was electrochemically determined that the H₂S impacted the FeCO₃ sufficiently to allow the general corrosion rate to increase.

Key words: Corrosion mechanisms, Corrosion rate, Hydrogen Sulfide, Oil and gas, Carbon dioxide

INTRODUCTION

A 2002 study estimated the annual cost associated with corrosion of gas pipelines to be around \$5 billion.¹ Corrosion of oil and gas pipelines continues to pose a major issue in the oil and gas industry due to the combination of brine produced with the oil and the type of acid gas present which can lead to significant internal corrosion. Oil and gas reservoirs can be separated into two categories, sweet and sour. In sweet reservoirs carbon dioxide (CO₂) is the dominant gas species that dissolves in the brine and hydrates to form carbonic acid which can increase the corrosion rate through a buffering effect but can also dissociate to react with ferrous ions to form corrosion product layers containing iron carbonate in the iron carbide matrix of the mild steel pipeline material. In sour reservoirs hydrogen sulfide (H₂S) is the dominant corrosive gas species, which similarly will dissolve in the brine and react with ferrous ions to form iron sulfide corrosion product layers associated with its presence, such as mackinawite. Understanding the characteristics of a reservoir is essential when planning how to appropriately mitigate the corrosion that

may occur, which includes material selection, inhibitor selection, and many other strategies. However, if a reservoir changes from sweet to sour, this can cause a large problem as the strategies previously selected and implemented may no longer be sufficient to control the corrosion. When H_2S begins to appear in a previously sweet reservoir, this is a phenomenon commonly known as souring. This can come about from a variety of pathways, the two most common being souring due to the presence of sulfate reducing bacteria (SRB) being unintentionally injected into the reservoir which then begin to produce H_2S . It is also possible that the SRB may already be present in the reservoir, but the injection water used may contain a high concentration of sulfate which then leads to the formation of H_2S . Regardless of how the reservoir begins to sour, it is important to understand what changes may occur once the souring has begun.

At the onset of souring the concentration of H_2S may remain relatively low for a significant period of time, meaning that the system will likely have whatever corrosion product layers had formed in the sweet corrosion system, being exposed to small concentrations of H_2S . Previous work has aimed at understanding the impact of low concentrations of H_2S in CO_2 systems, finding that the general corrosion rate decreases.^{2,3} Previous work has also shown that, under highly saturated conditions for iron carbonate and iron sulfide in a system containing both CO_2 and H_2S , it is possible to form a mixed layer. This same work also showed that under these conditions, the iron carbonate that was originally present as part of the corrosion product layer may disappear over time, which can be seen in the comparison of an X65 steel after a 1 hour exposure (Figure 1) and a 24 hour exposure (Figure 2).⁴

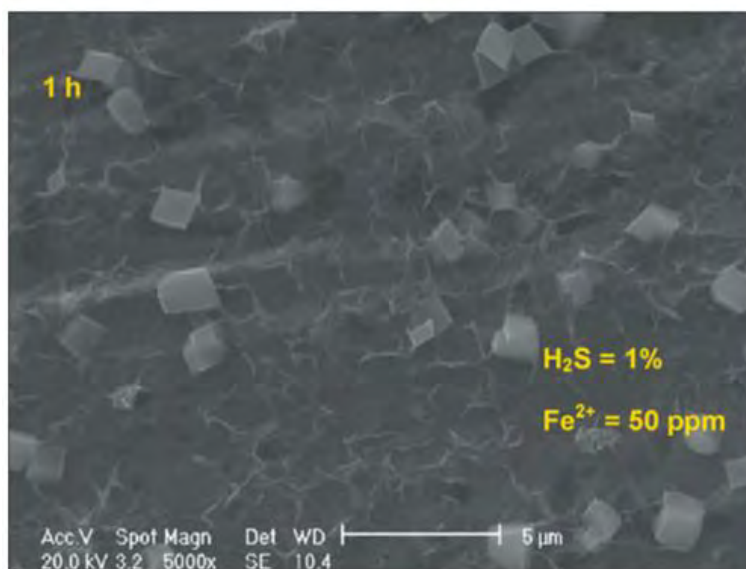


Figure 1. Mixed FeS and FeCO_3 layer in 1% H_2S with 50 ppm Fe^{2+} at 80°C , $\text{pH } 6.6 \pm 0.05$, 1 hour exposure.⁴

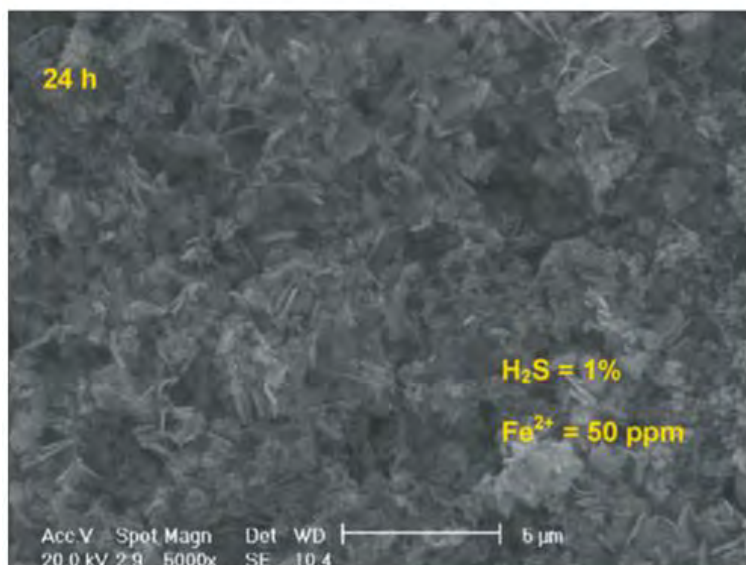


Figure 2. FeS layer in 1% H₂S with 50 ppm Fe²⁺ at 80°C, pH 6.6±0.05, 24 hour exposure.⁴

In Figure 1, iron carbonate crystals were precipitated on top of an iron sulfide layer that had formed within a 1-hour exposure time. However, in Figure 2, a sample from the same system extracted after 24 hours exposure shows only iron sulfide.

EXPERIMENTAL PROCEDURE

Experiments were conducted in a 2L glass cell filled with 1 wt% NaCl with 5 samples placed evenly around a central impeller allowing for similar flow conditions on all 5 samples, the glass cell setup can be seen below in Figure 3. Of the 5 samples present, one was capable of in-situ electrochemical measurements in conjunction with a Ag/AgCl reference electrode connected via Luggin capillary and a platinum coated mesh serving as the counter electrode. Two different sets of conditions were used in the data provided, in one the test cell was maintained at 1 bar, 30°C, and pH 4.0±0.05, and in the other the test cell was maintained at 1 bar, 80°C, and pH 6.6±0.05. The impeller, when used, was fixed at 75 rpm which provides flow properties to the samples similar to 1 m/s in a pipe with an inner diameter of 10 cm.

The results presented here involve experiments which can be separated into two stages. The first stage consists of the formation of a sweet corrosion product layer in the presence of pure CO₂, and in the second stage trace concentrations of H₂S will be introduced into the sparge gas. At the start of each experiment the glass cell setup would be sparged with pure CO₂ to remove oxygen from the glass cell. Solutions of hydrochloric acid or sodium bicarbonate would be used to adjust the pH to the desired value. The X65 metal samples would be polished using 600 grit SiC paper until no polishing marks were visible on the sample surface. The composition of the X65 steel can be seen below in Table 1. Once the samples were inserted into the system the desired iron carbonate corrosion product layer would be formed, then a sample would be extracted for analysis immediately prior to the introduction of the H₂S to have a baseline layer condition for comparison. Additional samples would be extracted throughout the exposure to H₂S to understand the development or changes in the corrosion product layer over time. The electrochemical sample would be used to take periodic linear polarization resistance (LPR) measurements to have an *in-situ* measurement of the general corrosion rate, as well as electrochemical impedance spectroscopy (EIS) measurements to determine solution resistance.

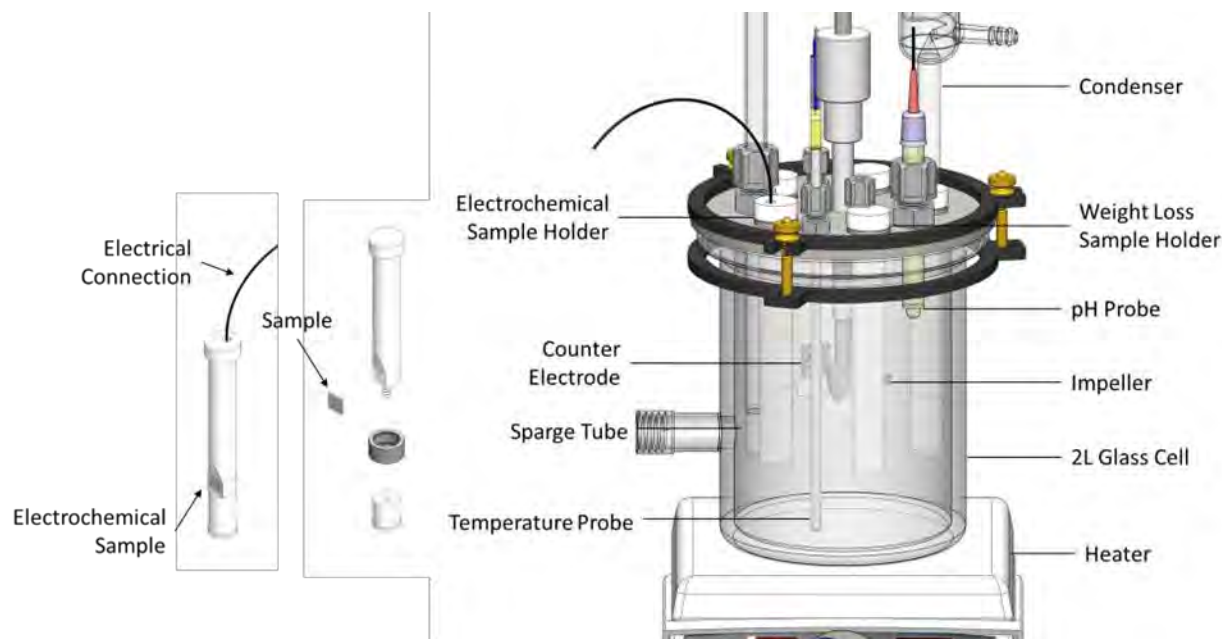


Figure 3. Glass cell setup used during experimentation.

Table 1. X65 steel composition

C	Mn	Nb	Si	V	Mo	Cu	Cr	Ni	Fe
0.05%	1.40%	0.04%	0.22%	0.03%	0.07%	0.11%	0.23%	0.24%	97.52%

Table 2. Experimental conditions

Parameter	Fe ₃ C Experiment	FeCO ₃ Experiment
Temperature	30°C (86°F)	80°C (176°F)
pH	4.00±0.05	6.60±0.05
Total pressure	1.01 bar (14.7 psi)	1.01 bar (14.7 psi)
Electrolyte	1 wt% NaCl	1 wt% NaCl
Impeller speed	75 rpm	0, 75 rpm
Equivalent pipe velocity	1 m/s (3.3 ft/s)	0, 1 m/s (3.3 ft/s)
Specimen	X65 steel	X65 steel
Gas phase components	CO ₂ and H ₂ S	CO ₂ and H ₂ S
Electrochemical methods	LPR, EIS	LPR, EIS
H ₂ S _(g) concentration	60 ppm	80 ppm
Layer formation time	72 hours	48 hours
Total test time	144 hours	114 hours

EXPERIMENTAL RESULTS

Exposure of an iron carbide layer (Fe₃C) to slightly sour environment

First, testing conducted to first form an iron carbide layer before the introduction of H₂S will be reviewed, the conditions for the formation can be found in Table 2 (Fe₃C Experiment). The iron carbide layer was formed over 72 hours in pure CO₂ saturated solution at pH 4.0±0.05 and 30°C with an impeller speed of 75 rpm. After the formation of the iron carbide layer, 60 ppm H₂S in the gas phase was introduced to the system, all other parameters remained constant. The experiment continued with the 60 ppm H₂S for a further 72 hours before the experiment was concluded. The corrosion rate obtained from the *in situ* LPR measurements over the duration of the experiment can be seen below in Figure 4.