Effects of Sodium Chloride Concentration on Mild Steel Corrosion in Slightly Sour Environments

H. Fang,* B. Brown,** and S. Nešić*

ABSTRACT

A research project was conducted to investigate the effect of a high salt concentration on corrosion from low partial pressures of hydrogen sulfide (H$_2$S). The main objective was to study if the high concentration of chloride could initiate localized attack in this type of H$_2$S system. Experiments were conducted in a nitrogen-purged system with a trace amount of H$_2$S (50 ppm) in the gas phase. Only weight loss was used to measure corrosion rates. Scanning electron microscopy (SEM) and energy-dispersive x-ray (EDX) methods were used to characterize the corrosion products. Experimental results show that a high salt concentration significantly slowed down the reaction rate in H$_2$S corrosion. Some pitting attack was found both in salt-free and high salt conditions, but experimental results did not show evidence that chlorides can initiate localized corrosion in low pH$_2$S systems.

KEY WORDS: carbon dioxide corrosion, carbon steel, chloride concentration, hydrogen sulfide, inclusions, localized corrosion, pitting attack

INTRODUCTION

The severity of hydrogen sulfide (H$_2$S, sour) corrosion problems in oil and gas production is increasing as fields age and H$_2$S is produced progressively more. Pitting corrosion along the bottom of the pipeline is the primary corrosion factor leading to failure of sour gas pipelines. It has been suggested that the kinetics of H$_2$S corrosion is controlled by the nature of corrosion product film in terms of both phase type and morphology. Local breakdown of iron sulfide (FeS) films is suspected to be the main factor in the initiation of localized H$_2$S corrosion. Breakdown of FeS films may be a result of environmental factors, such as the effect of solids, chlorides, sulfur, high velocity, among others.

Severe pitting corrosion has been observed in field failures of both wells and pipelines when there are very high concentrations of H$_2$S and chlorides present. However, few laboratory studies of the chloride effect on localized H$_2$S corrosion have been published in the open literature. Consequently, the role of chlorides in localized H$_2$S corrosion is poorly understood. The present study was directed to fill a part of this gap by conducting experiments at high salt concentrations (10 wt% sodium chloride [NaCl]) and low concentrations of H$_2$S. This study is part of a Chemical Engineering Ph.D. research program on the "Mechanisms of Elemental Sulfur Corrosion" with the ultimate objective of observing if a high concentration of chloride (using NaCl) can initiate localized areas of corrosion attack on a thin iron sulfide corrosion product film.

EXPERIMENTAL PROCEDURES

An experimental plan was defined to investigate the high salt concentration effect on H$_2$S corrosion. Experiments were conducted in salt-free deionized water and at high salt (10 wt%) concentrations. The test matrix is shown in Table 1.
**Tests in Deionized Water**

H₂S corrosion experiments were performed first in a salt-free condition. The purpose of this experiment was to determine whether localized corrosion could be

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**Experimental Setup**

The experimental setup is shown in Figure 1. The 50-ppm concentration of H₂S in nitrogen (N₂) was made by the dilution of a 500-ppm H₂S/N₂ gas mixture with 99.9% purity nitrogen through a rotameter. The 50-ppm H₂S concentration in the gas phase was confirmed by sampling the gas entering the test solution with a H₂S colorimetric tube at atmospheric pressure. Experiments were performed in a glass cell filled with 2 L of deionized (DI) water at the desired salt concentration (0 or 10 wt%). The temperature was controlled by a hot plate with a thermocouple in the solution. Initially, the test cell was deoxygenated by purging with nitrogen. After that, the diluted H₂S gas was introduced and the system was purged continu-

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**Specimen Preparation**

The same type of carbon steel, C1018 with the composition shown in Table 2, was used in all the experiments. Specimens were polished with silicon carbide (SiC) sand paper prior to being tested. The 240-, 400-, and 600-grit sand paper was used sequentially. After polishing, specimens were immersed in an ultrasonic cleaner with isopropyl alcohol ([CH₃]₂CHOH) for 1 min to 2 min, and then air dried.

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**RESULTS AND DISCUSSION**

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**TABLE 1**

*Test Matrix for H₂S Experiments*

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total pressure</td>
<td>1 bar</td>
</tr>
<tr>
<td>H₂S concentration</td>
<td>50 ppm</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>NaCl solution</td>
<td>0 wt%, 10 wt%</td>
</tr>
<tr>
<td>Initial pH</td>
<td>5.0</td>
</tr>
<tr>
<td>Material</td>
<td>C1018</td>
</tr>
</tbody>
</table>

**TABLE 2**

*Chemical Composition of C1018 Carbon Steel (wt%)*

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Mn</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>0.38</td>
<td>0.09</td>
<td>0.05</td>
<td>0.05</td>
<td>0.01</td>
<td>Balance</td>
</tr>
</tbody>
</table>

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(1) UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE International) and cosponsored by ASTM International.
initiated in the absence of chlorides, i.e., when carbon steel specimens have been exposed only to a H₂S environment for an extended period of time.

Figure 2 shows the change in corrosion rate with time. The low corrosion rates observed suggest that an iron sulfide film formed immediately on the metal surface and gave protection. Figure 3 shows the pH and iron concentration change with time. The pH increased significantly from 5 to 7 after one day then remained stable at around 7. The ferrous ion concentration in the solution was measured at around 1 ppm. This suggests that most of the dissolved iron generated by the corrosion process was converted to an insoluble iron sulfide film.

The molar concentrations of the species under the test conditions with DI water, Table 3, can be calculated using Henry's law constant⁶ for the determination of H₂S(aq) concentration, and a previously reported physicochemical model⁶ defines the constants used to determine molar concentrations of H⁺, HS⁻, OH⁻, and S²⁻. The concentration of H₂S(aq) is constant at different pH because of the continuous purging of the 50-ppm H₂S/N₂ mixed gas, but the dominant species in solution changes from [H⁺] at pH 5 to [HS⁻] at pH 7. In contrast, ferrous ion (Fe²⁺) concentrations are a product of the corrosion reaction on the steel samples and must be measured. Since the Fe²⁺ concentration in solution is affected by the amount of iron sulfide that forms, this concentration can vary with time (Figure 3).

Table 3. Calculated Species Bulk Solution Concentrations at 25°C, 100 ppm H₂S in 1 bar N₂

<table>
<thead>
<tr>
<th>Species in Solution</th>
<th>Molar Concentrations at pH 5</th>
<th>Molar Concentrations at pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>1.0 x 10⁻⁶ M</td>
<td>1.0 x 10⁻⁷ M</td>
</tr>
<tr>
<td>H₂S(aq)</td>
<td>4.2 x 10⁻⁶ M</td>
<td>4.2 x 10⁻⁶ M</td>
</tr>
<tr>
<td>HS⁻</td>
<td>4.4 x 10⁻⁸ M</td>
<td>4.4 x 10⁻⁸ M</td>
</tr>
<tr>
<td>OH⁻</td>
<td>9.0 x 10⁻¹⁶ M</td>
<td>9.0 x 10⁻¹⁶ M</td>
</tr>
<tr>
<td>S²⁻</td>
<td>3.8 x 10⁻³⁰ M</td>
<td>3.8 x 10⁻¹⁶ M</td>
</tr>
</tbody>
</table>

(A) Dominant species for corrosion reactions.

Surface Analysis After Different Exposure Times

1 Day — A SEM picture of the bare metal before exposure is shown in Figure 4 to enable comparisons with the surface morphology of corrosion specimens after the experiment. Figure 5 shows the SEM image and EDX spectrum of a specimen surface after a 1-day exposure. A very thin layer was formed on the specimen surface, and the film appeared to be fragmented. EDX data show that sulfur and iron are the main components of the films, consistent with the formation of iron sulfide.
Sufficiently thin that the polishing marks can readily be observed. The iron sulfide film was removed with a Clarke solution. The final surface morphology is shown in Figure 7. EDX analysis confirmed that the iron sulfide film had been removed from the surface.
No initiation of localized corrosion was observed under this condition.

6 Days — After 6 days’ exposure to H₂S, iron sulfide film became much thicker (Figure 8). A new feature can be observed: iron sulfide “blooms,” which formed on top of the more-or-less uniform iron sulfide film. EDX analysis shows that the sulfide content of the bloom is much higher than that of the uniform sulfide film; however, this could be an artifact related to the EDX technique. SEM image of the specimen surface after film removal is shown in Figure 9. At several points, what appears to be pitting attack was observed on the metal surface. The diameter of these small pits varied from 6 μm to 15 μm. A 3D-software
reconstruction of SEM images was used to analyze the pit depth. Figure 10 shows the 3D view of one such pit. The pit depth is approximately 40 μm so the corresponding time-averaged pitting rate is calculated to be ~2.4 mm/y. Compared with the general corrosion rate of 0.017 mm/y, the localized corrosion rate is more than two orders of magnitude higher.

12 Days — The iron sulfide film kept growing with time. Iron sulfide "blooms" formed on the metal surface in greater quantity (Figure 11). The composition of the iron sulfide "bloom" at 12 days was similar to the one at 6 days. After film removal at 12 days’ exposure, pitting corrosion again was observed. The pitting density at 12 days was higher than that seen at 6 days (Figure 12). More and more small pits were observed after the corrosion product was removed by Clarke’s solution. The deepest pit depth observed was around 14 μm (Figure 13), suggesting that the pit size change was not happening over time; in other words, no pit propagation was detected.
Why Did Pitting Attack Initiate and Not Propagate?

As stated above, some pitting (localized corrosion) was observed on the specimen surface even in the salt-free test conditions. Exposed specimens were reexamined using SEM and EDX to try to establish the reason of pitting initiation. Figure 14 shows one location of the specimen surface without the iron sulfide films at 6 days' exposure to a salt-free solution at 25°C, showing what appears to be a bead of a different material at the bottom of the pit. This occurred at several locations. EDX results confirmed the presence of aluminum and magnesium inside the pits. It is suspected that these may have been present as inclusions in the parent steel or were introduced by the surface-polishing process. The feasibility of the first assumption was confirmed by looking at steel composition and consulting a metallurgist. The second assumption needed further investigation. Figure 15 shows a freshly prepared bare metal surface polished by sand paper—aluminum and magnesium were also found at a few locations. Gold sputter-coated sand paper was analyzed using EDX and the same elements were found (Figure 16), confirming that the metal inclusion in the steel may have been related to specimen preparation.

It can be hypothesized that pitting was initiated as a result of the presence of inclusions in the steel surface since the pit density was observed to increase with time, yet the examination of a freshly prepared surface had very few indications of the suspect elements on the steel surface. Observations signify that once the steel around the inclusions was dissolved away sufficiently, the inclusions were removed and
pit propagation stopped. However, more experimental verification is needed to confirm this hypothesis with a future research goal to include the study of the links between material inclusions and pitting.

10 wt% NaCl — In the second series of experiments, the salt concentration was increased to 10 wt% to investigate the effect of high chloride concentrations on localized H₂S corrosion of carbon steel. Similar pitting corrosion attack was also observed in high salt conditions as was seen at salt-free conditions described above. However, the higher salt concentration significantly decreased the uniform corrosion rate (Figure 17) as well as the pitting corrosion rate.

Surface Analysis After Different Exposure Times

1 Day — Figure 18 shows the SEM image of the specimen surface after 1 day exposure to H₂S at 10 wt% NaCl, 25°C. There is barely any iron sulfide film formed on the metal surface in comparison to similar observations in salt-free conditions. The high salt concentration also greatly retarded the uniform corrosion rate as measured by weight loss. A significant quantity of NaCl is observed in the SEM, crystallized on the metal surface because of the rapid dehydration of the specimen by alcohol upon retrieval from the glass cell.

3 Days — In this case, the corrosion specimen was rinsed first with deoxygenated, DI water to remove NaCl after retrieval from the glass cell; therefore, no NaCl crystals were observed on the specimen
CORROSION SCIENCE SECTION

This series of tests was conducted to investigate the effect of a high salt concentration on corrosion from low partial pressures of $H_2S$. Surface analysis and weight-loss measurements of mild steel samples were used to clarify this effect on general corrosion and localized corrosion scenarios.

According to the experimental results, it appears that a high salt concentration (10 wt%) significantly retarded the overall general corrosion reaction rate of mild steel in the presence of a small amount of $H_2S$ (50 ppm in the gas phase at 1 bar). Figure 26 shows the comparison of localized and general corrosion rates with different salt concentrations at 25°C and 50 ppm $H_2S$ after 12 days. Results show that an increase in the salt concentration decreased both the

CONCLUSIONS

- This series of tests was conducted to investigate the effect of a high salt concentration on corrosion from low partial pressures of $H_2S$. Surface analysis and weight-loss measurements of mild steel samples were used to clarify this effect on general corrosion and localized corrosion scenarios.

- According to the experimental results, it appears that a high salt concentration (10 wt%) significantly retarded the overall general corrosion reaction rate of mild steel in the presence of a small amount of $H_2S$ (50 ppm in the gas phase at 1 bar). Figure 26 shows the comparison of localized and general corrosion rates with different salt concentrations at 25°C and 50 ppm $H_2S$ after 12 days. Results show that an increase in the salt concentration decreased both the

surface. Thicker iron sulfide film was observed after the corrosion specimen was exposed to $H_2S$ for 3 days (Figure 19). However, the FeS film was not uniform.

7 Days — Blooms in the iron sulfide film appeared on the specimen surface (Figure 20), which are more concentrated when compared with the films observed at 7 days in salt-free conditions. However, the rest of the film is relatively thin. The general corrosion rate at high salt concentration condition is still very low. Some pitting attack was evident after the film was removed by Clarke’s solution (Figure 21). However, the pits were too small to quantify in depth.

15 Days — The morphology of iron sulfide films at 15 days was similar to the film morphology observed at 7 days (Figure 22). The difference is that the iron sulfide film at 15 days was visibly thicker as suggested by the SEM image. Figure 23 shows the SEM image of the specimen surface without iron sulfide films at 15 days. Some pitting attack was observed, and a 3D analysis of the pit is shown in Figure 24.

26 Days — Figure 25 shows the iron sulfide film morphology after the corrosion specimen was exposed to $H_2S$ for 26 days. Some major cracks of the iron sulfide films were observed. Large and deep pits were expected; however, no severe pitting corrosion was observed after the iron sulfide film was removed.
general corrosion rate and the localized corrosion rate under these conditions.

Pitting corrosion initiation was observed in both salt-free and high-salt concentration conditions; however, no propagation of the pits was observed. Steel inclusions and other imperfections were expected to have caused the initiation of localized attack to the carbon steel in this series of experiments. Therefore, the initial hypothesis that chlorides would initiate and lead to severe localized corrosion (pitting) in a slightly sour environment was not confirmed by these experiments. However, the role of chloride ions on initiation of localized corrosion in sour systems simply cannot be excluded. The presence of chlorides is an indi-
cation of an increase in solution conductivity. This increase may not affect the general corrosion rate, but is expected to affect localized corrosion initiation and propagation influenced by environmental conditions. Further research possibilities on this topic are to include higher H$_2$S concentrations, higher temperatures, and complicating effects of CO$_2$. 

**FIGURE 22.** Corrosion specimen exposed to H$_2$S for 15 days at 10 wt% NaCl, 25°C, with film.

**FIGURE 23.** Corrosion specimen exposed to H$_2$S for 15 days at 10 wt% NaCl, 25°C, without film.

**FIGURE 24.** Three-dimensional view of corrosion specimen exposed to H$_2$S for 15 days at 10 wt% NaCl, 25°C, without film.
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REFERENCES


FIGURE 25. Corrosion specimen exposed to H₂S for 26 days at 10 wt% NaCl, 25°C, with film.

FIGURE 26. Comparison of localized and general corrosion rates with different salt concentrations at 25°C, 50 ppm H₂S, 12 days.

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