

Investigation of Elemental Sulfur Corrosion Mechanisms

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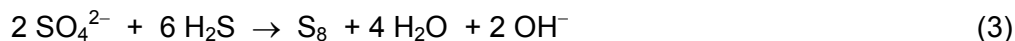
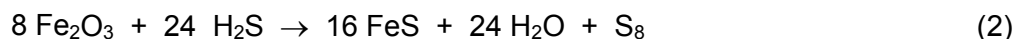
Sour gas wells frequently co-produce elemental sulfur which can cause catastrophic corrosion of mild steel. As producing wells become increasingly sour, the incidence of sulfur corrosion will likely increase. Despite the severity of this problem, limited mechanistic information about this process exists in the literature. The objective of this study is investigation of the corrosion mechanism involving elemental sulfur.

Building on the knowledge found in open literature, sulfur hydrolysis and the sulfur/iron reaction mechanisms were both studied in this work. It was found that a sulfur hydrolysis reaction does occur during elemental sulfur corrosion, but does not appear to be dominant. Experimental results confirmed that a sulfur/iron electrochemical reaction is the main mechanism of elemental sulfur corrosion.

Keywords: elemental sulfur corrosion, hydrolysis, electrochemical reaction

INTRODUCTION

The primary source of elemental sulfur in sour gas wells is the oxidation of hydrogen sulfide. This may occur as a result of ingress of oxygen, the presence of reducible high oxidation state metals, such as ferric ion in iron(III) oxide, or be related to reservoir thermochemical sulfate reduction¹⁻³:



In each of the above reactions the sulfur has been represented as S₈, corresponding to its stable/dominant allotrope at temperatures approaching 160°C; note that it is molten at temperatures above 115°C (α -sulfur).^{4,5} Other possible sulfur formation processes include H₂S dissociation at elevated temperatures or microbial sulfate reduction.^{6,7}

Typically, elemental sulfur is carried by the sour gas from the production zone well casing to the pipeline. However, as pressures and temperatures decrease, this sulfur will deposit. In aqueous conditions, contact of sulfur with mild steel has resulted in the onset of catastrophic corrosion processes.^{8,9}

A series of experiments have been performed to investigate the elemental sulfur corrosion mechanism. The study began with a sulfur hydrolysis test and preliminary corrosion measurements, these results were reported at CORROSION2008.¹⁰ In the hydrolysis experiments, sulfur was mixed with de-oxygenated DI water in a glass cell or autoclave at different temperatures (25°C, 60°C, 80°C, 125°C, 150°C). The pH was monitored during the experiments and was recorded after it became stable which usually required a few hours. According to the experimental results shown in Figure 1, it appeared that the sulfur reacted with water at temperatures exceeding 80°C, resulting in slight acidification of the solution. The stabilized pH values were significantly higher than those reported in a similar study by Maldonado-Zagal and Boden.¹¹ In a similar study performed by Schmitt¹², and consistent with our experiments, no significant pH drop was observed. In both of these studies, hydrogen sulfide and sulfuric acid were suspected to be the sulfur hydrolysis reaction products. However, there was no experimental evidence to confirm this hypothesis.

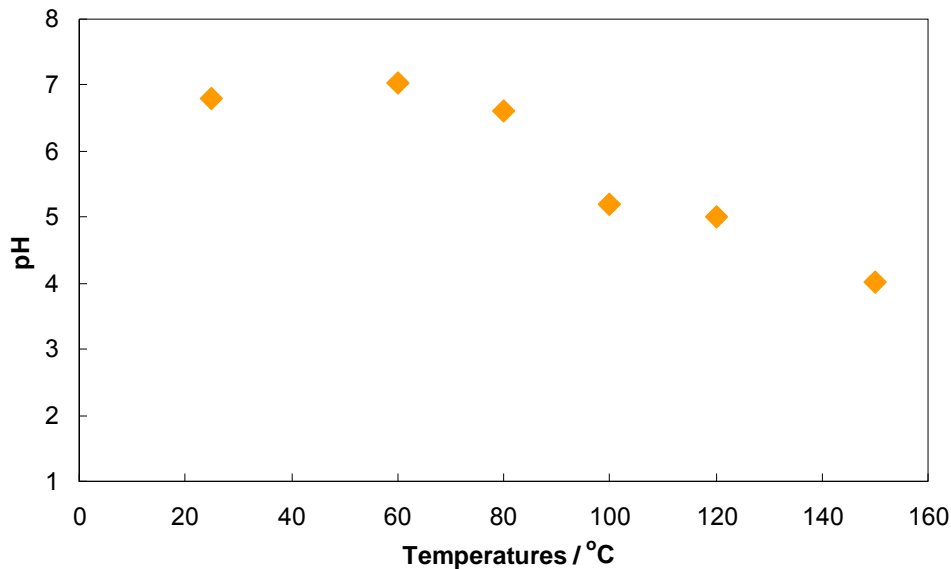


Figure 1. pH at equilibration after mixing water with sulfur at various temperatures.

The current study is comprised of two complementary sections: a further in-depth look at sulfur hydrolysis that was followed by an investigation of the nature of the direct sulfur/iron reaction. Overall, the final objective is to further elucidate the elemental sulfur corrosion mechanism.

EXPERIMENTAL

Sulfur Hydrolysis

Sulfur hydrolysis experiments were conducted in a sealed autoclave at different temperatures. Sulfur was weighed and then put in a glass Petri dish. Approximately 1 gram of sulfur was used for each experiment. This was then transferred to an autoclave filled with 500 ml DI water. Nitrogen was then purged through the solution to facilitate deoxygenation. After 40 minutes of purging, the autoclave was pressurized to 300 psi and heated to the desired temperature. After 24 hours, the autoclave was depressurized and the test solution sampled. During the depressurizing process, a GASTEC™ pump with a colorimetric tube was used to determine the possible presence of hydrogen sulfide in the gas phase. The reaction solution was sampled and analyzed by ion chromatography to identify the ion species present in the test solution after equilibration. The system was cooled down to room temperature and the pressure released. pH measurements were conducted after each test at 30°C.

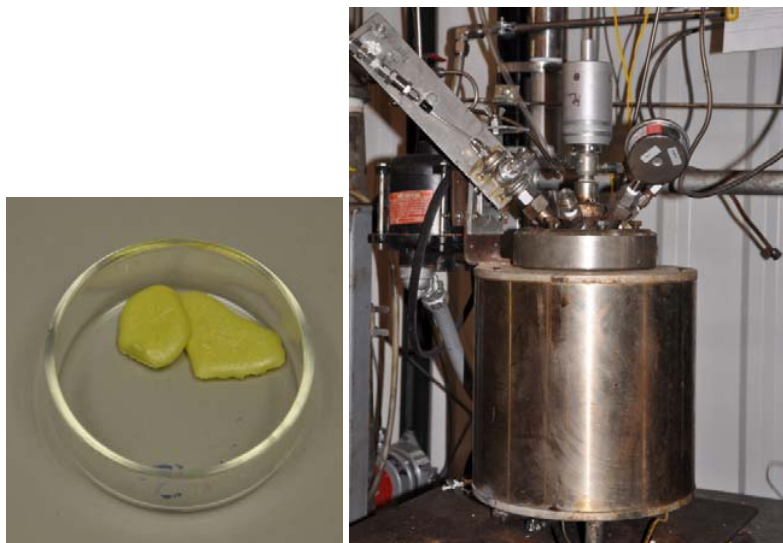


Figure 2. Sulfur in a glass Petri dish and the autoclave used in the sulfur hydrolysis experiments.

Direct sulfur/iron reaction

In this entire series of experiments, sublimed elemental sulfur (ACROS 99.999%) was deposited onto polished samples by heating it slightly above its melting-point (115°C) then pouring it onto the sample surface (X65 steel). Previous research¹⁰ on this type of sample had been conducted in both nitrogen purged DI water with and without sodium chloride.

Severe corrosion attack was observed underneath the sulfur droplet in every case. Interestingly, in DI water most of the corrosion occurred under the area where sulfur and steel have direct contact. Based on this observation, it was assumed that the direct reaction between sulfur and iron was the dominant reaction during the corrosion process. However, after salt was added to the test solution, the corrosion attack on the steel spread out beyond the sulfur droplet covering the entire metal sample surface. The weight loss corrosion rate also increased. This suggested that the presence of chloride ions played an important role in the corrosion process and also indicated that electrochemical reactions may underpin elemental sulfur corrosion. However, to further confirm the electrochemical nature of elemental sulfur corrosion, new experiments needed to be designed and conducted.

In the new experiments, either an electrically insulating or conductive barrier was placed between the sulfur droplet and the metal sample surface, separating the steel and sulfur from direct contact. The design of these experiments was meant to reveal the mechanisms of sulfur corrosion by distinguishing the importance of two main parameters: direct physical proximity vs. electrical contact of sulfur and steel. The barriers placed between the sulfur droplet and sample surface in three different series of tests were: a non-conductive nylon mesh, and a conductive graphite sheet with and without an array of small holes (Figure 3). Samples thus prepared were then transferred to a glass cell for corrosion experiments. Glass cell tests were performed in a salt free and a 1.5M salt solutions (NaCl).

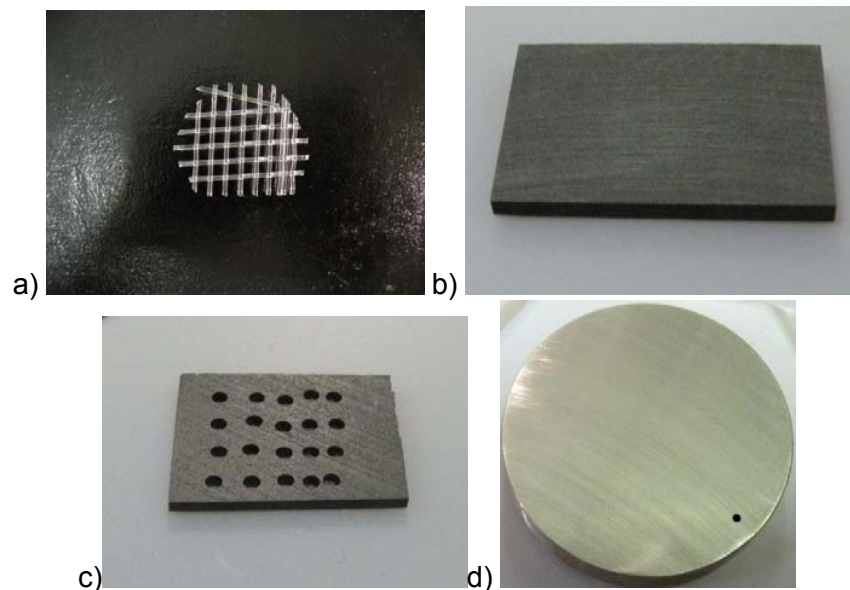


Figure 3. Materials used for the physical separation of sulfur and iron: a) plastic mesh, b) graphite sheet, c) graphite sheet with 0.043" ID holes, d) X65 steel sample.

After removal from the glass cell following the experiment, corrosion samples were immediately put into deoxygenated deionized water to dissolve any soluble salts from the sample surface. Prior to surface analysis, the unreacted sulfur was mechanically removed from the sample surface. Samples were characterized by scanning electron microscopy (SEM), energy dispersive X-ray fluorescence microanalysis (EDX) and infinite focus microscopy (IFM). Corrosion products were then removed by treatment with Clarke solution¹² and the bare corroded steel sample surface was re-characterized by IFM. Localized corrosion rates were determined by analysis of IFM data whereas general corrosion rates were obtained by weight loss methods.

RESULTS AND DISCUSSION

Sulfur hydrolysis

Ion chromatography results: sulfuric acid had previously been proposed to be the product of the sulfur hydrolysis reaction¹¹; therefore, a standard solution with aqueous sulfate ion (SO_4^{2-}) was first prepared and tested by ion chromatography to obtain a standard chromatogram for comparison with data obtained from the experimental solutions. The results are shown in Figure 4. Sulfate ion appeared at a retention time of 8.3 minutes. In order to avoid contamination of the chromatography column by the standard solution, pure DI water was injected into the instrument to clean the column. Figure 5 shows the results for DI water after column purging, note the absence of any SO_4^{2-} peak in the chromatogram. This confirmed that the column was free from SO_4^{2-} and ready for reinjection.

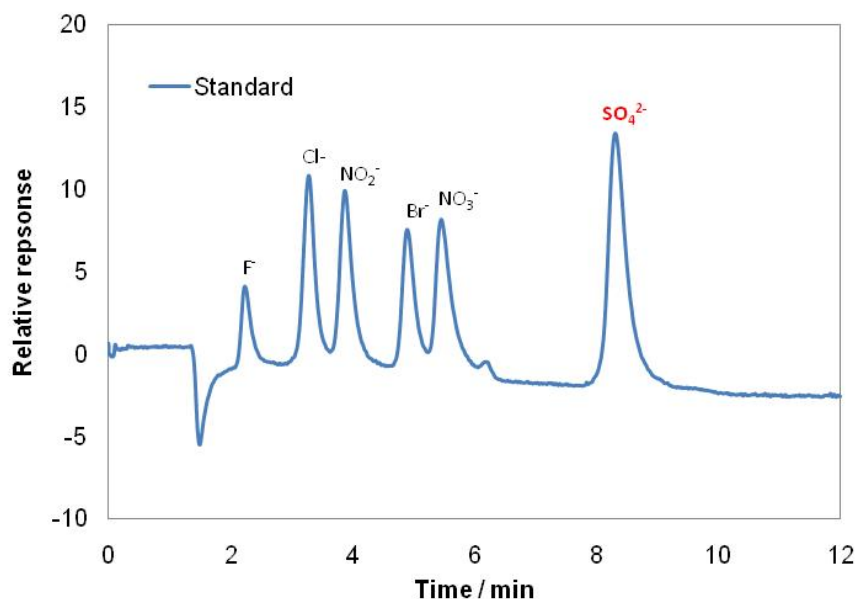


Figure 4. Chromatogram for standard solution with SO_4^{2-} .

Figure 6 shows the chromatogram for different test solutions recovered at various temperatures (25°C, 80°C, 135°C and 150°C) after equilibration. These results indicate that sulfate ions are present in all test solutions and that the concentration increases with temperature (peak area increases with increase of temperature). This qualitatively indicates that sulfuric acid, H_2SO_4 , is a likely product of sulfur hydrolysis. Interestingly, hydrogen sulfide was only detected at 150°C and the concentration was extremely low (less than 1 ppm). This may be because the reaction rate is low and insufficient gaseous hydrogen sulfide was generated for detection in lower temperature tests.

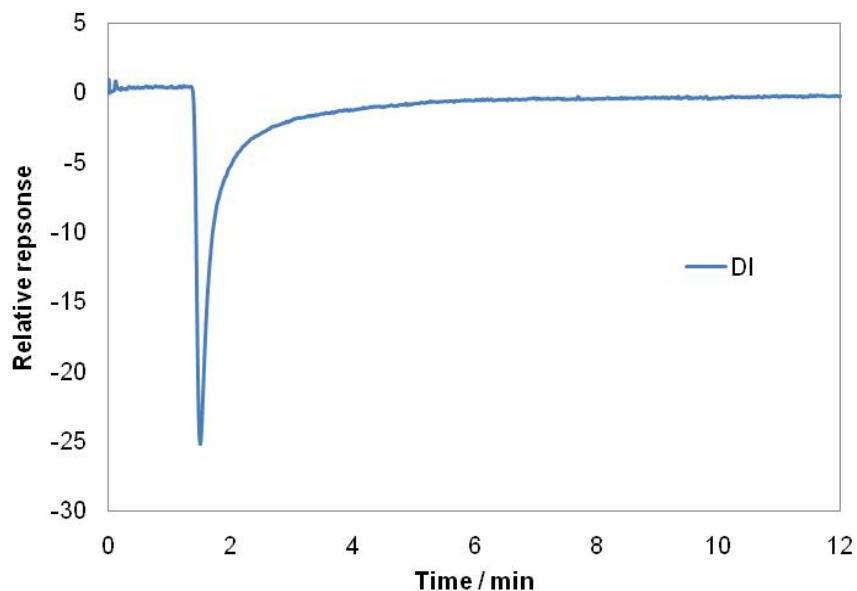


Figure 5. Chromatogram for DI water after purging of the chromatographic column.

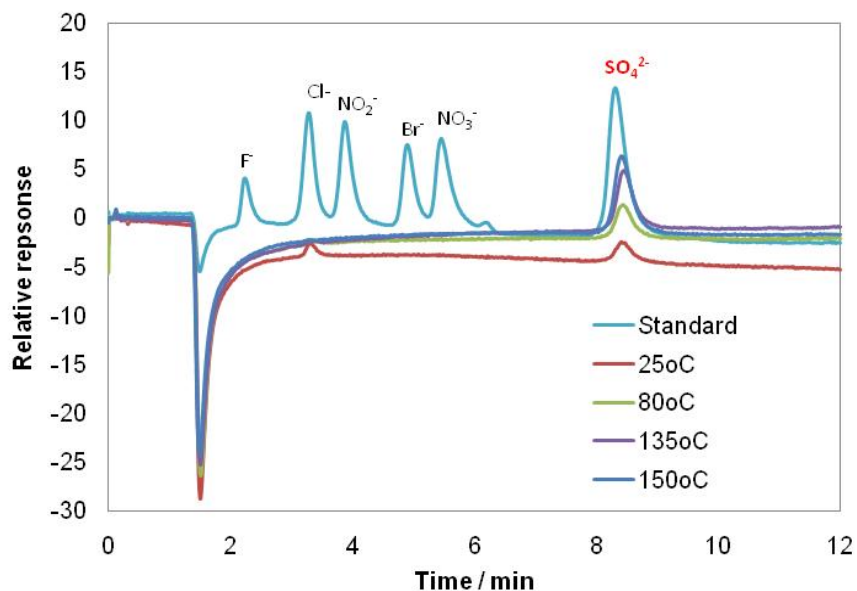


Figure 6. Chromatograms for water/sulfur solutions exposed at different temperatures.

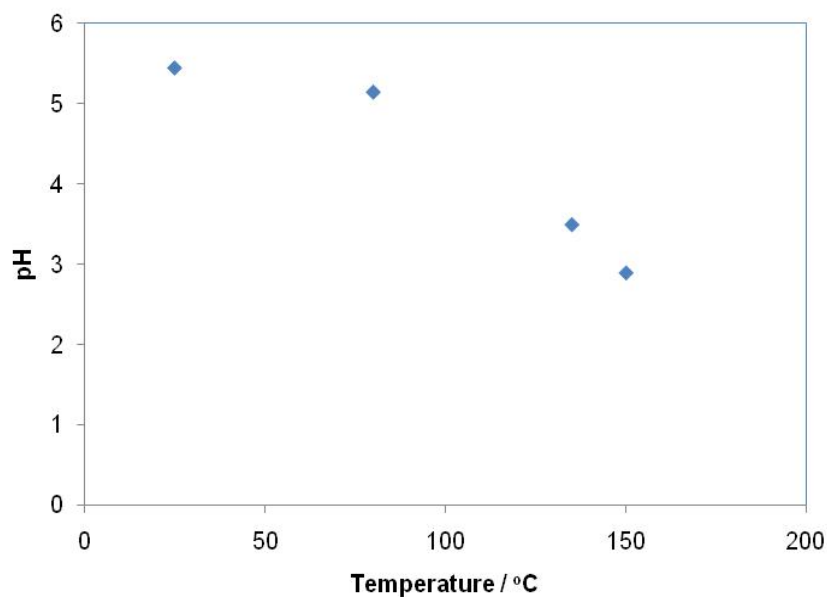


Figure 7. pH of the test solution after degassing for the studied temperatures.

The pH measurements after each 24 hour experiment at different temperatures are shown in Figure 7. The pH value of 2.9 observed at 150°C strongly suggests the presence of a strong acid in the test solution. According to the chromatography results that showed the presence of SO_4^{2-} , the acid is believed to be sulfuric acid (H_2SO_4). Although no hydrogen sulfide was detected in the gas phase, hydrogen sulfide and sulfuric acid are still considered to be the most likely products of the sulfur hydrolysis reaction, therefore one can write:



Direct sulfur/iron reaction

Experiments with the plastic mesh. A plastic mesh was placed between the sulfur droplet and the sample surface (Figure 8). By doing that, sulfur was both physically separated (if only for a small distance) and electrically insulated from the steel sample surface. The thickness of the mesh is about 2 mm, which still puts the sulfur and the sample in close proximity to each other.

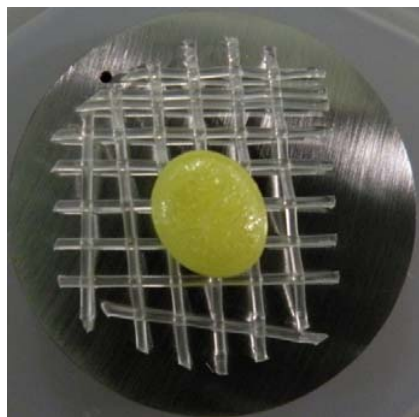


Figure 8. Sample arrangement for the sulfur/plastic-mesh/steel test, where steel surface is in close proximity to sulfur but electrically insulated from it.

The experiment was conducted at 25°C in pH neutral de-ionized water. Figure 9 shows a picture of the sample surface after 1 day. The sulfur and plastic mesh were physically removed from the sample surface. A slight black tarnish was observed on the sample surface. Figure 10 shows the SEM/EDX data for a typical region of the sample surface. The surface morphology is similar to a steel surface exposed to a solution containing a very small amount (traces) of dissolved hydrogen sulfide. EDX data also indicates an small amount of sulfur. This would be consistent with the hypothesis that a small amount of hydrogen sulfide was generated by the sulfur hydrolysis reaction and its subsequent reaction with the steel surface.

From a series of similar experiments it was concluded that when the sulfur and steel sample were in physical proximity but electrically insulated from each other, corrosion was not measurable and virtually no corrosion product film was obtained. This suggests that the physical proximity between sulfur and steel alone is insufficient to cause corrosion attack.



Figure 9. Steel sample surface after exposure in the sulfur/plastic-mesh/steel test where it was in close proximity to sulfur but electrically insulated from it.

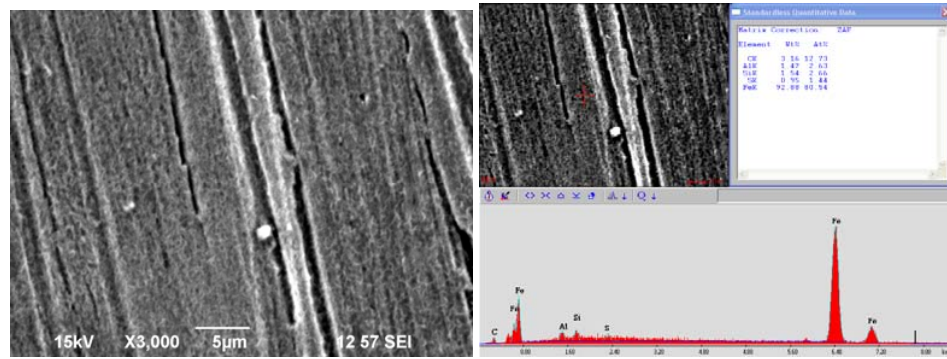


Figure 10. SEM/EDX data for the typical corroded steel surface after exposure in the sulfur/plastic-mesh/steel test where it was in close proximity to sulfur but electrically insulated from it.

Experiments with the carbon sheet. In this series of experiments, the sulfur and a steel surface were physically separated but electrically connected by placing an electrically conductive carbon sheet (2mm thick) between them (Figure 11). This experiment was also conducted at 25°C in pH neutral DI water. A picture of the sample surface after corrosion is shown in Figure 12.

A thin tarnish layer formed on the sample surface but only in the area which was covered by the carbon sheet. However, corrosion attack under this condition was not severe. The surface region which was uncovered by the carbon sheet remained untarnished and shiny, which suggests that essentially no corrosion occurred in this area. **Error! Reference source not found.** shows the SEM/EDX data of the surface underneath the carbon sheet. EDX data suggests that most of the film observed in the area covered by the carbon sheet was a mixture of iron oxide and iron sulfide.

This series of experiments suggested that if the steel surface and sulfur are physically separated but electrically connected, the sulfur will be reduced, the iron will be oxidized and iron sulfide will form in between the two. However, because of the separation and due to the impermeability of the carbon sheet, it was difficult for the reactive species to diffuse through, and therefore the degree of attack was not high. It was concluded that electrical connection between sulfur and steel alone does not lead to a severe corrosion attack.

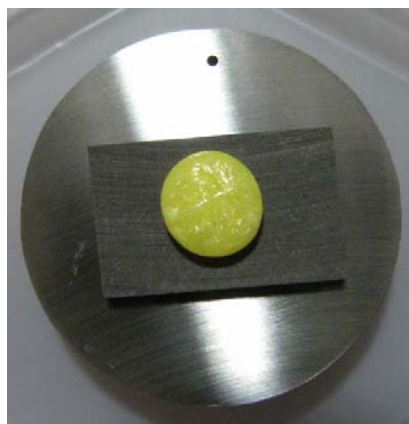


Figure 11. Sample arrangement for sulfur/carbon-sheet/steel test where the steel was separated from the sulfur but electrically connected to it.

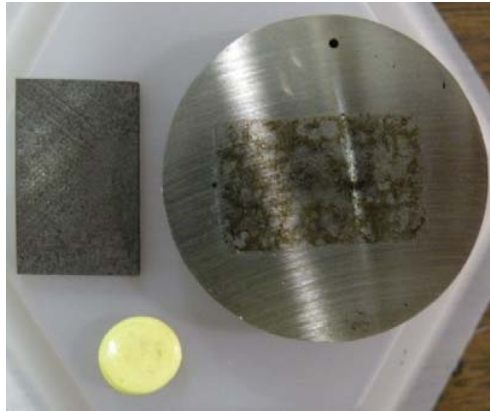


Figure 12. Steel sample surface after exposure in the sulfur/carbon-sheet/steel test where the steel was separated from the sulfur but electrically connected to it.

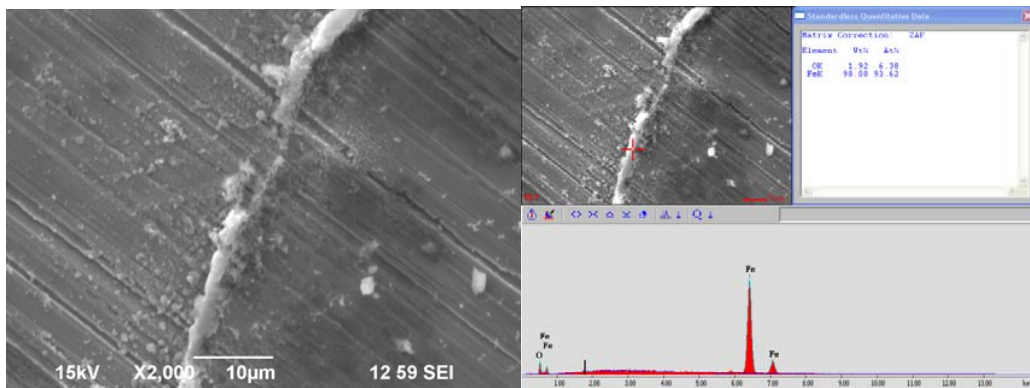


Figure 13. SEM/EDX data for the steel sample surface underneath the carbon sheet after exposure in the sulfur/carbon-sheet/steel test where the steel was separated from the sulfur but electrically connected to it.

Experiments with the carbon sheet with holes. This experiment was meant to investigate the case when sulfur was both electrically connected and in physical proximity to the steel surface. Figure 14 shows the sample arrangement.

The experiment was again conducted at 25°C in pH neutral DI water. After the experiment, the sulfur and carbon sheet were physically removed from the sample surface. Figure 15 shows the SEM/EDX data for the sample surface beneath a hole. It is apparent that a thin layer of corrosion product formed on the area directly under the hole. EDX data confirmed this to be an iron sulfide.

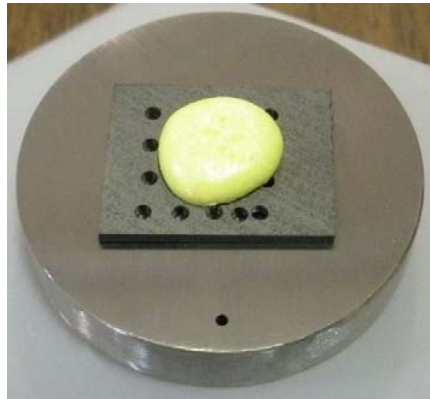


Figure 14. Sample arrangement for sulfur/carbon-sheet-with-holes/steel test where the steel was in physical proximity to the sulfur and electrically connected to it.

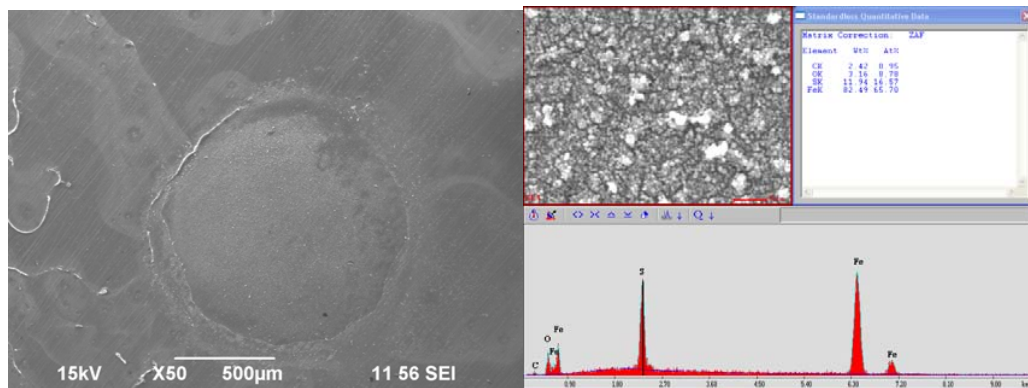


Figure 15. SEM/EDX data for the sample surface underneath the hole from the experiment where the steel was in physical proximity to the sulfur and electrically connected to it.

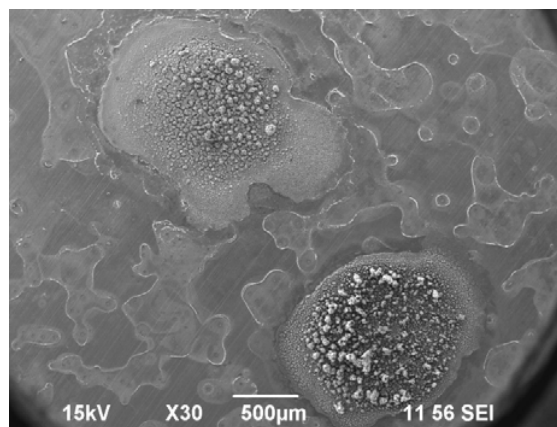


Figure 16. SEM data for the sample surface underneath the hole, from the experiment where the steel was in physical proximity to the sulfur and electrically connected to it.

Figure 16 shows a SEM image of another location of the specimen surface after the experiment. It is clearly seen that iron sulfide film was mostly generated on the specimen

surface directly underneath the holes. This is different from what was observed when the plastic mesh or the carbon sheet without holes was used. The experimental results indicate that when the carbon sheet provided a conductive media for the electron transfer between sulfur and steel and the holes enables the mass transfer of species, and the degree of attack was much higher.

In another experiment, the temperature was increased to 80°C to increase the kinetics of the corrosion reaction. Figure 17 shows the SEM image of the sample surface underneath the carbon sheet with holes. A significant amount of sulfide film was observed directly under the holes. In this case, much more severe corrosion occurred on the metal surface.

From the above investigation, it was concluded that elemental sulfur corrosion can occur without direct contact of sulfur and the steel surface. Severe corrosion may occur when sulfur and steel are electrically connected and in physical proximity to each other. This investigation revealed the electrochemical nature of elemental sulfur corrosion.

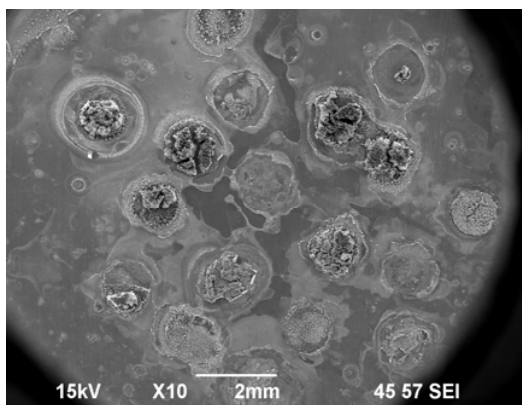


Figure 17. SEM image of the sample surface underneath the carbon sheet with holes from the higher temperature experiment where the steel was in physical proximity to the sulfur and electrically connected to it.

CONCLUSIONS

- Significant sulfur hydrolysis occurs only at elevated temperatures.
- The electrical connection and physical proximity between sulfur and steel are critical characteristics for elemental sulfur corrosion of mild steel.
- An electrochemical reaction is the likely mechanism of elemental sulfur corrosion of mild steel.

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