

CORROSION OF MILD STEEL IN THE PRESENCE OF ELEMENTAL SULFUR

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ABSTRACT

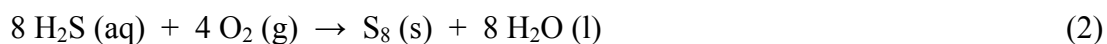
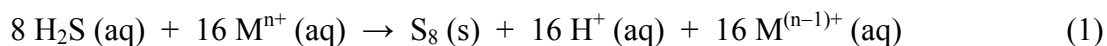
Elemental sulfur is often produced by sour gas wells, primarily due to the oxidation of hydrogen sulfide. This may occur as a result of oxygen contamination. Alternatively, with pressure and temperature changes in the line, sulfur may precipitate and deposit on the pipeline walls. In the presence of water, contact of solid sulfur with mild steel can result in the onset of catastrophic corrosion processes.

The objective of this project is to study the effect of elemental sulfur on the corrosion of mild steel. In preliminary experiments, elemental sulfur hydrolysis and sulfur-mild steel corrosion were investigated. Sulfur was found to react with water at temperatures of greater than 80°C, resulting in significant acidification of the corrosion solution. It was also found that elemental sulfur can cause localized corrosion of mild steel when they are in direct contact. Iron sulfide films/scales readily formed on the surface of the steel; these were analyzed by infinite focus microscopy (IFM), scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Keywords: Elemental sulfur, mild steel, iron sulfide, sulfur hydrolysis, localized corrosion

INTRODUCTION

Elemental sulfur can readily form in aqueous systems *via* the oxidation of sulfide species.¹ Possible reactions for the formation of elemental sulfur (S₈) could involve high oxidation state metals (denoted Mⁿ⁺) or oxygen:



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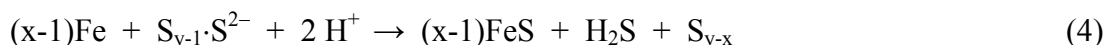
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In addition to strictly chemical processes, sulfide oxidizing bacteria have been shown to form liquid sulfur droplets under ambient conditions.² Consequently, the formation of elemental sulfur is almost inevitable in H₂S corrosion environments in the field. Elemental sulfur is shown as S₈ in the reaction equations below as that represents the stable allotrope of sulfur under standard conditions.

Acidification in sulfur containing aqueous systems has been reported, with species such as H₂S, H₂SO₂, H₂SO₃, H₂SO₄ and polysulfides being possible candidates as hydrolysis products.³ Maldonado-Zagal and Boden⁴ proposed that acid formation as a result of sulfur hydrolysis was the main factor governing corrosion in the presence of elemental sulfur:



Alternatively, MacDonald *et al.* hypothesized that an electrochemical reaction between iron and polysulfide is the driving force for corrosion in systems where elemental sulfur is present.^{5,6}



The objective of this project is to study the effect of elemental sulfur on the corrosion of mild steel, with particular emphasis on detection of pH effects, identification of formed corrosion products, study of pitting phenomena and measurement of general/localized corrosion rates.

EXPERIMENTAL PROCEDURE

Experiments were conducted to determine temperature effects on the acidification of pure water with elemental sulfur. This involved adding elemental sulfur to deoxygenated deionized water purged with nitrogen and measuring the pH of each test system with time. The chosen temperature range was 25-150°C. Experiments were conducted in both glass cells and autoclaves.

For the corrosion experiments, elemental sulfur (ACROS 99.999%) was deposited onto polished coupons by heating it slightly above its melting-point (115°C) then pouring it onto the coupon surface (C1018 steel). This gave uniform coverage of adherent sulfur to the coupon surface. Care was taken not to oxidize the sulfur as it was heated.

Coupons thus prepared were then transferred to a glass cell for corrosion experiments. Conditions for the elemental sulfur corrosion experiments are summarized in the test matrix outlined in Table 1.

Corrosion coupons were removed from the glass cell and characterized after 1, 4 and 5 days. Prior to analysis, unreacted sulfur was mechanically removed from the coupon surface. Samples were characterized with a JEOL6390LV scanning electron microscope (SEM), EDAX energy dispersive X-ray fluorescence attachment (EDX), Alicona infinite focus microscope (IFM) and Rigaku Geigerflex X-ray diffractometer (XRD); XRD data was taken from films directly on the corrosion coupons. Corrosion products were then removed by treatment with Clarke solution, ASTM standard G1 section 7.7.2 approved by ASTM committee April 24 1981, and the corrosion coupons recharacterized by IFM. Localized corrosion rates were determined by analysis of IFM data whereas general corrosion rates were obtained by weight loss methods.

RESULTS

Acidification of water with elemental sulfur

Significant acidification of water upon exposure to elemental sulfur was measurable only at temperatures in excess of 80°C, as shown in Figure 1. The pH values shown there were obtained after waiting for at least a few hours while the measured pH stabilized. The results confirmed that hydrolysis products were indeed being formed by reaction of elemental sulfur with water, be they H₂S, H₂SO₂, H₂SO₃, H₂SO₄ and/or polysulfide species. The pH values measured were significantly higher than those reported in a similar study by Maldonado-Zagal and Boden⁴, however it is difficult to establish why. Also, it is not clear if this mechanism can be used as an explanation for localized attack on mild steel by elemental sulfur, as the lowest pH values observed fall within the typical range of pH seen in water/CO₂ systems.

Elemental sulfur corrosion experiments

A coupon with elemental sulfur on the surface prior to exposure is shown in Figure 2. The portion of the coupon surface which was in direct contact with the elemental sulfur was significantly blackened after exposure; this was due to the formation of iron sulfide. A typical coupon surface, after the reaction, is shown in Figure 3.

Representative SEM/EDX data for the corrosion coupon surface that has been in direct contact with elemental sulfur for one day at 25°C is shown in Figure 4. Note that most of the surface film resembles a blistered layer (top left SEM image). Cracking of the film shown in the enlarged image, reveals that it is very thin, which seems to be exfoliating from the surface. A further enlargement of the small area shows that the film appears amorphous, with no well defined morphologies present; this was confirmed by XRD. The composition of the film was shown to consist of iron sulfide by using EDX. The IFM image of the corrosion coupon after the iron sulfide has been removed reveals some pitting corrosion, Figure 5. The top right image corresponds to the small region marked on the “whole coupon” picture to the left of it. The line across the “twin pits” corresponds to the profile data at the bottom of the figure. Note that the first pit has a depth of *ca.* 18 μm whereas the second pit is *ca.* 12 μm. Comparison of general and localized corrosion rate data of generated samples is given below. After four days at 25°C a thicker film has formed at the surface, see Figure 6. The exfoliation of the film is obvious on the enlarged image on the top right. The origin of the lines on the underside of the exfoliated film are due to the polishing marks on the original steel substrate, which have left an imprint on the sulfide film formed by a solid state reaction. Cracking of the film is more severe on this coupon than the one exposed for only one day. From EDX and XRD, it is clear that the film chemistry remains fundamentally unchanged in the longer exposure. Film pit depths appear similar to those observed after 1 day; however, the profile shown in Figure 7 seems to indicate a broadening effect. After a 5 day exposure at 25°C, see Figure 8, the films seem to be even thicker and coarser than before, but pit depth remains similar, see Figure 9.

Another similar series of experiments was conducted at 80°C. After one day at 80°C there is a much thicker film present on the coupon surface than was observed at 25°C, see Figure 10. Distinct iron sulfide microcrystallites seem to have formed. The pitting depth is again about 15 μm, see Figure 11. After 4 days at 80°C, Figure 12, the film has become thicker and coarser, appearing more crystalline. Pitting depth remains at *ca.* 15 μm, Figure 13, but broadening is again observed. Pit density on the surface also appears to be increasing. After 5 days at 80°C, Figure 14, the entire surface seems to be covered by a coarse and cracked film. From XRD, the dominant phase is the crystalline iron sulfide

mackinawite, see Figure 15. Mackinawite is a layered structure which is common in aqueous environments under mildly sour conditions.⁷

Comparison of general and localized corrosion rates are shown in Figures 16 and 17. Both refer to the steel surface area underneath the elemental sulfur deposit. At 25°C, the localized corrosion rate (pitting) decreased from 7.2 mm/yr after one day to 1.7 mm/yr after 5 days. The general corrosion rate remained essentially unchanged at *ca.* 0.80 mm/yr. At 80°C, the localized corrosion rate was 5.1 mm/yr after one day, but was reduced to 3.0 mm/yr after 5 days. The general corrosion rate was 1.6 mm/yr at 80°C, double the general corrosion rate measured at 25°C.

It is worth noting that the thick deposits of iron sulfide on the steel substrate formed directly beneath the elemental sulfur. Consequently, a direct solid-state reaction for the formation of iron sulfide from elemental precursors is a more likely process which may occur in these systems:



Such a reaction path does not depend on the generation of acidic species when water is exposed to elemental sulfur.

CONCLUSIONS

- Significant acidification of water by its reaction with sulfur did not occur at temperatures lower than 80°C. This mechanism is thought to be less significant than the direct reaction of elemental sulfur with the steel surface.
- Corrosion product films generated by the direct reaction of elemental sulfur with C1018 steel were confirmed to be iron sulfide. Corrosion films became progressively thicker with time. Little change was observed in general corrosion rate with time. Pitting rates were significantly higher than the general corrosion rates.

ACKNOWLEDGEMENTS

The authors would like to thank the sponsor companies of the Corrosion Center Joint Industry Project for the support of this research.

TABLES

TABLE 1
TEST MATRIX FOR ELEMENTAL SULFUR CORROSION EXPERIMENTS

Parameter	Conditions
Total Pressure	1 bar
Temperature	25, 80°C
Solution	0 wt.% NaCl
pH	7
Material	C1018

FIGURES

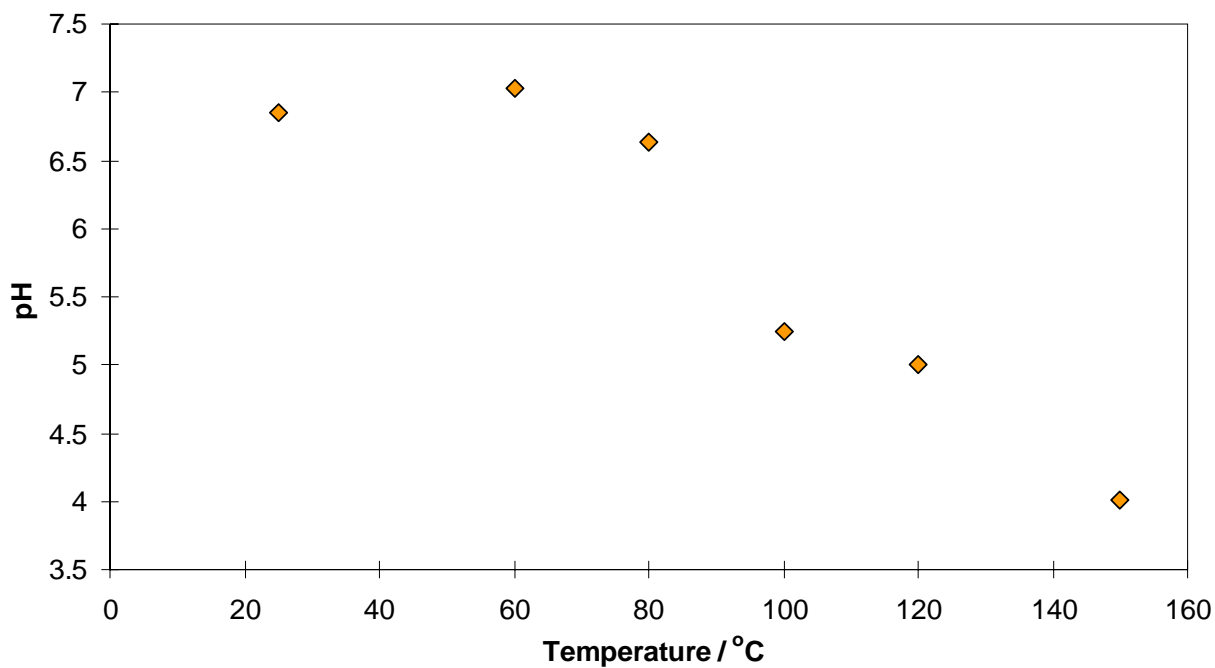


FIGURE 1 – Acidification of water by its reaction with elemental sulfur at different temperatures.



FIGURE 2 – Elemental sulfur deposited on the surface of a corrosion coupon before exposure.



FIGURE 3 – The overall surface of a corrosion coupon after exposure to elemental sulfur (25°C, 3 days).

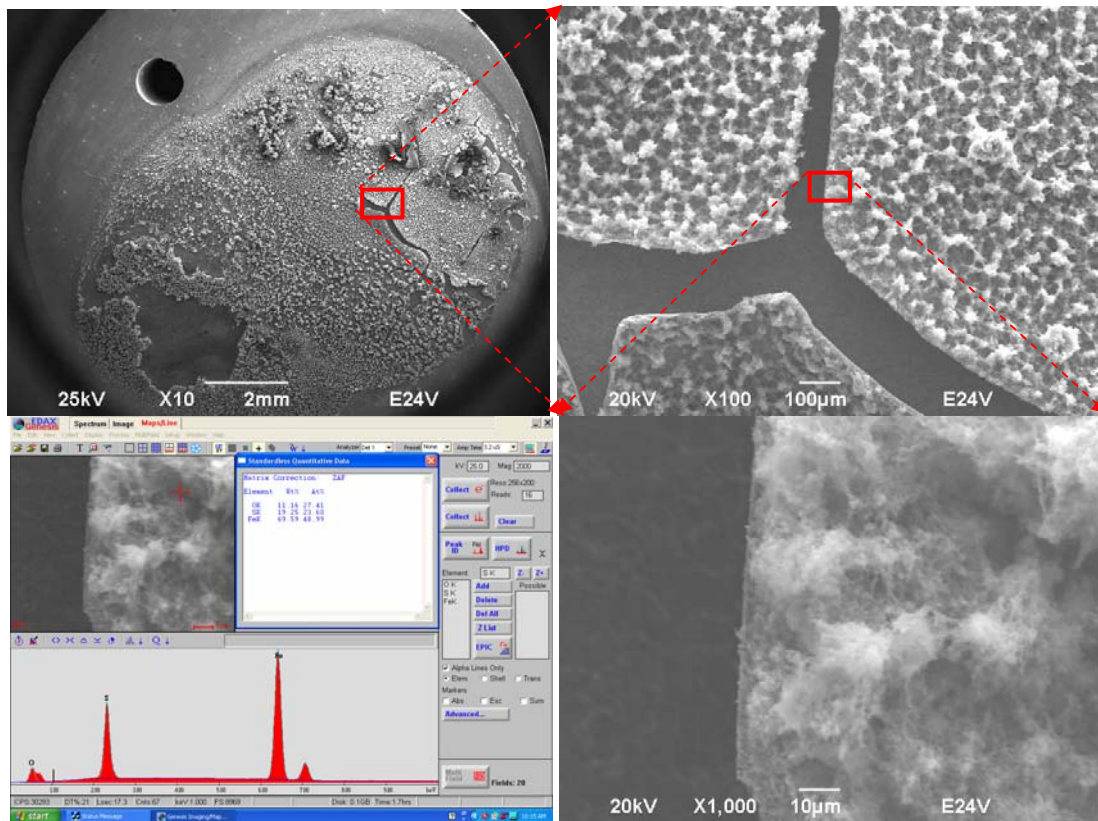


FIGURE 4 – Corrosion coupon contacted with elemental sulfur for 1 day at 25°C, with film.

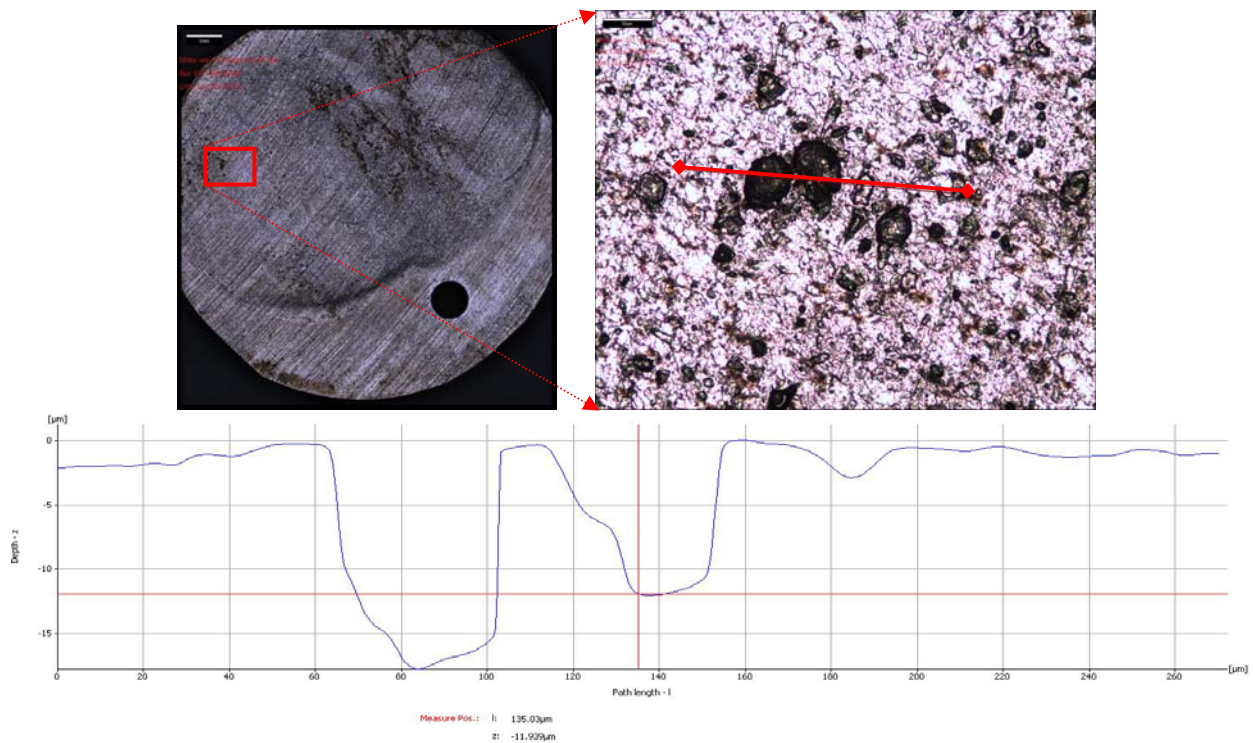


FIGURE 5 – IFM data for corrosion coupon contacted with sulfur for 1 day at 25°C, without film, appearance of the surface (top images) and a line profile.

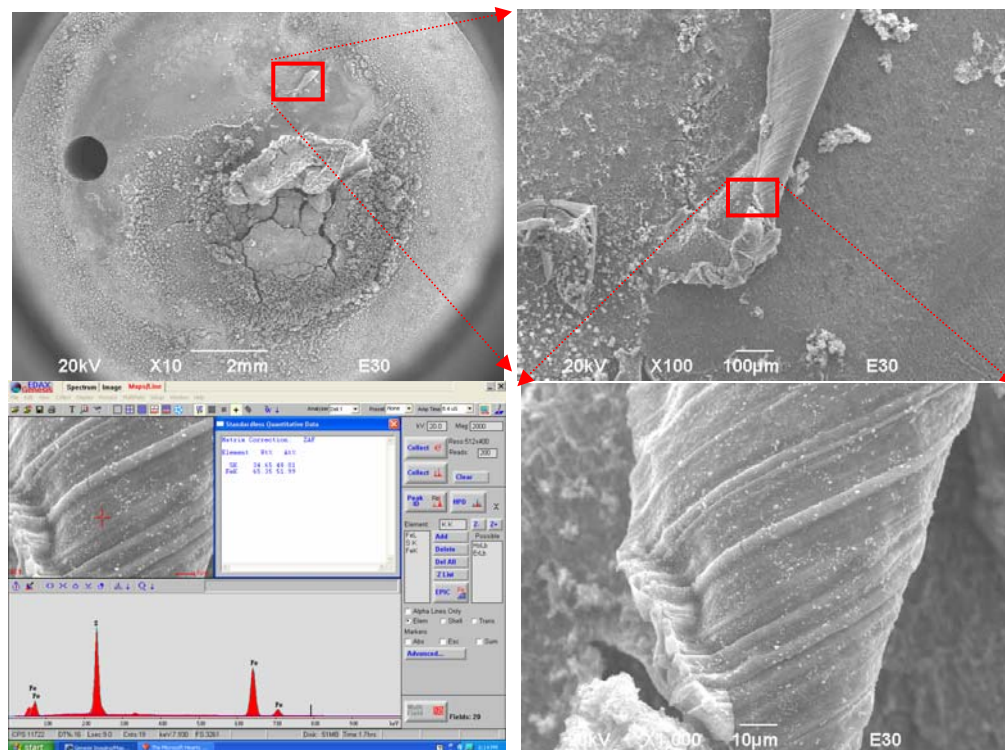


FIGURE 6 – Corrosion coupon contacted with elemental sulfur for 4 days at 25°C, with film.

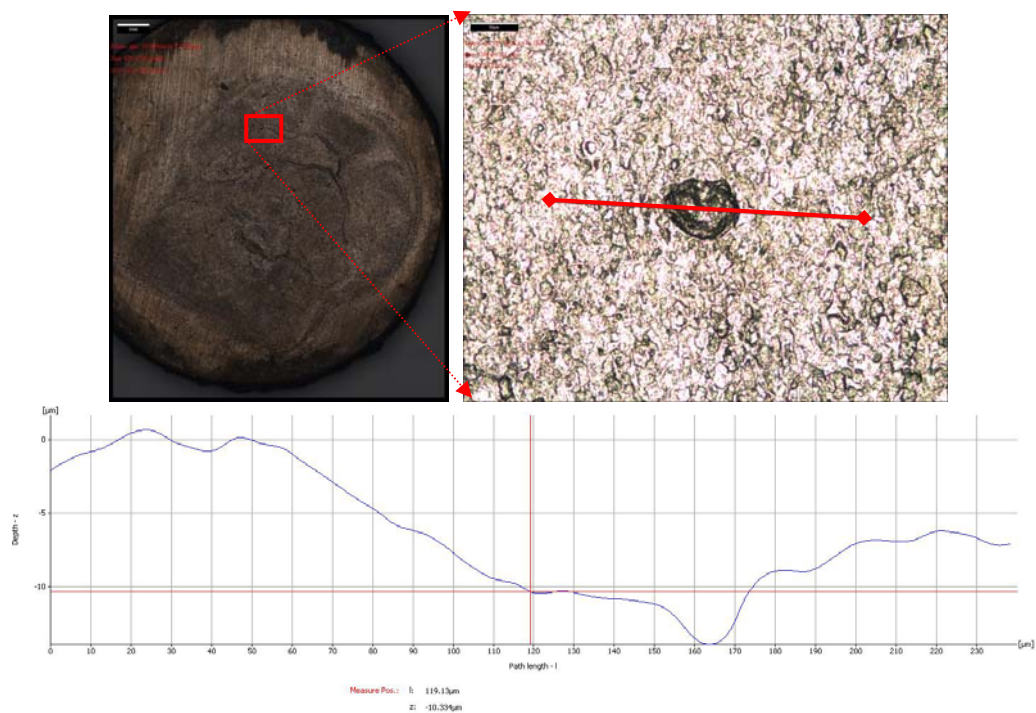


FIGURE 7 – IFM data for coupon contacted with sulfur for 4 days at 25°C, without film.

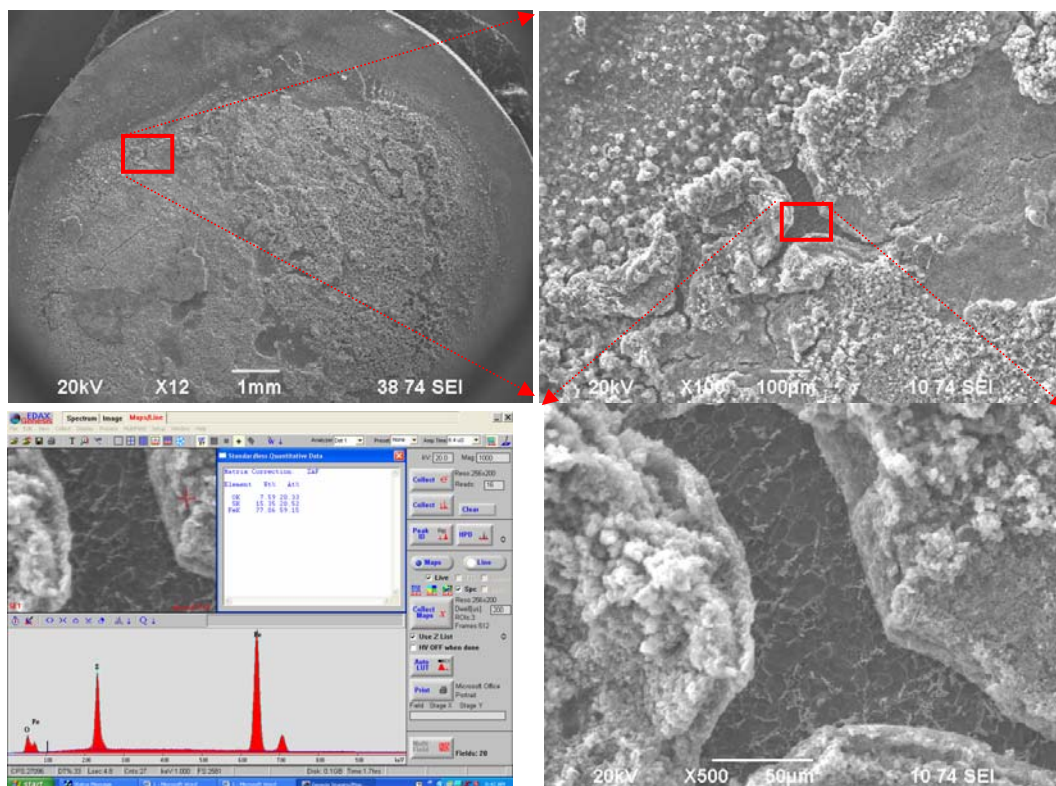


FIGURE 8 – Corrosion coupon contacted with elemental sulfur for 5 days at 25°C, with film.

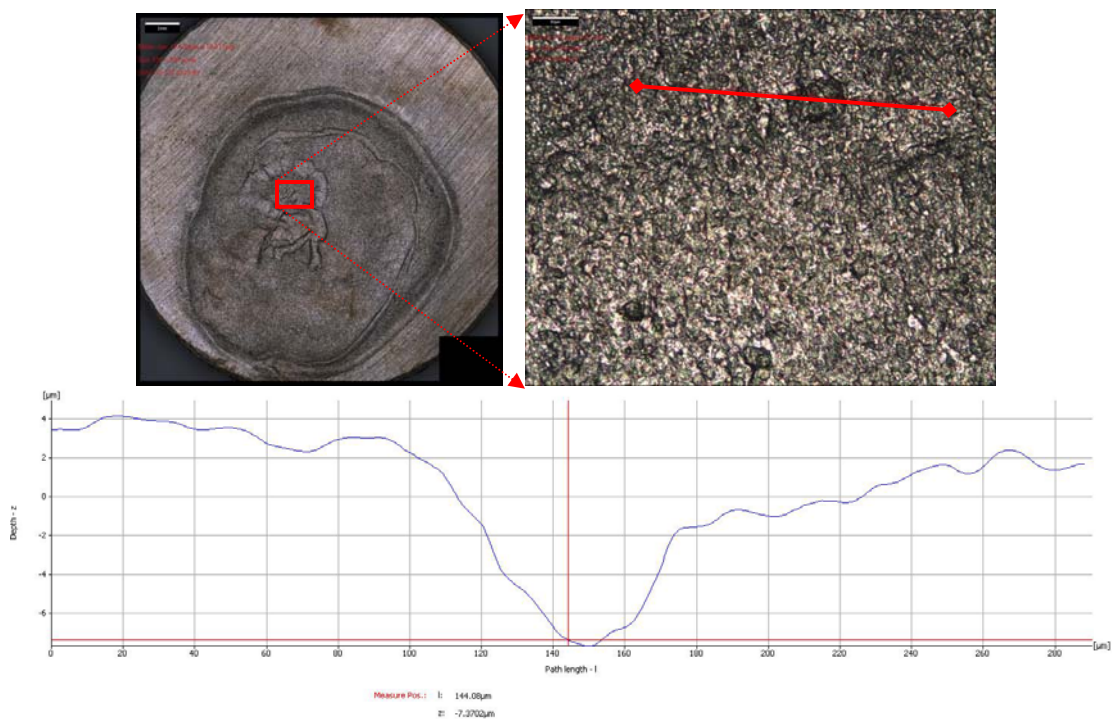


FIGURE 9 – IFM data for coupon contacted with sulfur for 5 days at 25°C, without film.

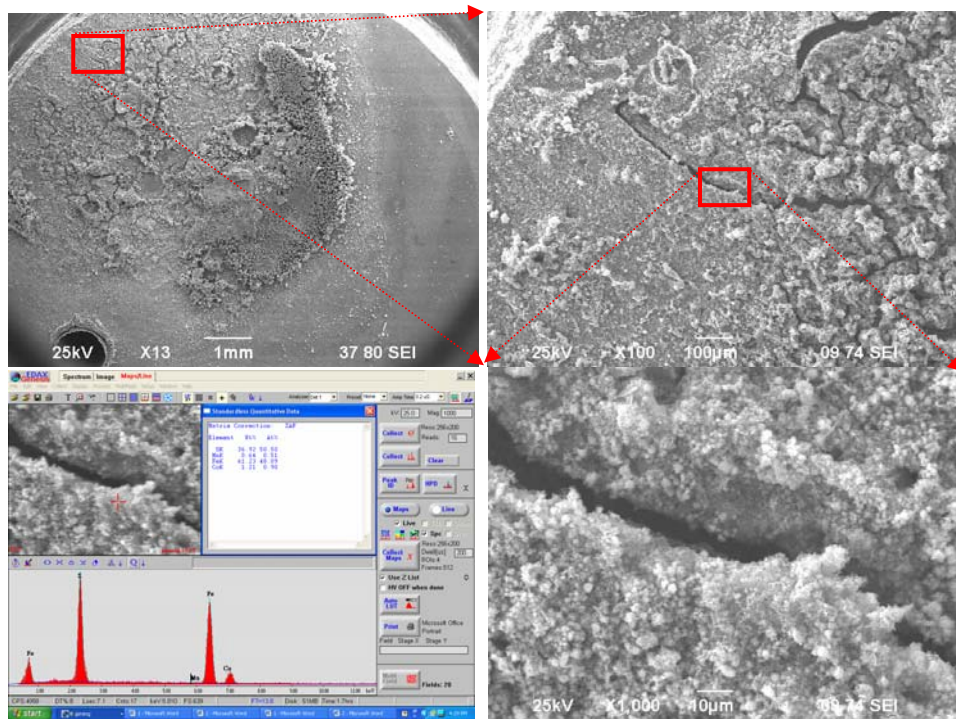


FIGURE 10 – Corrosion coupon contacted with elemental sulfur for 1 day at 80°C, with film.

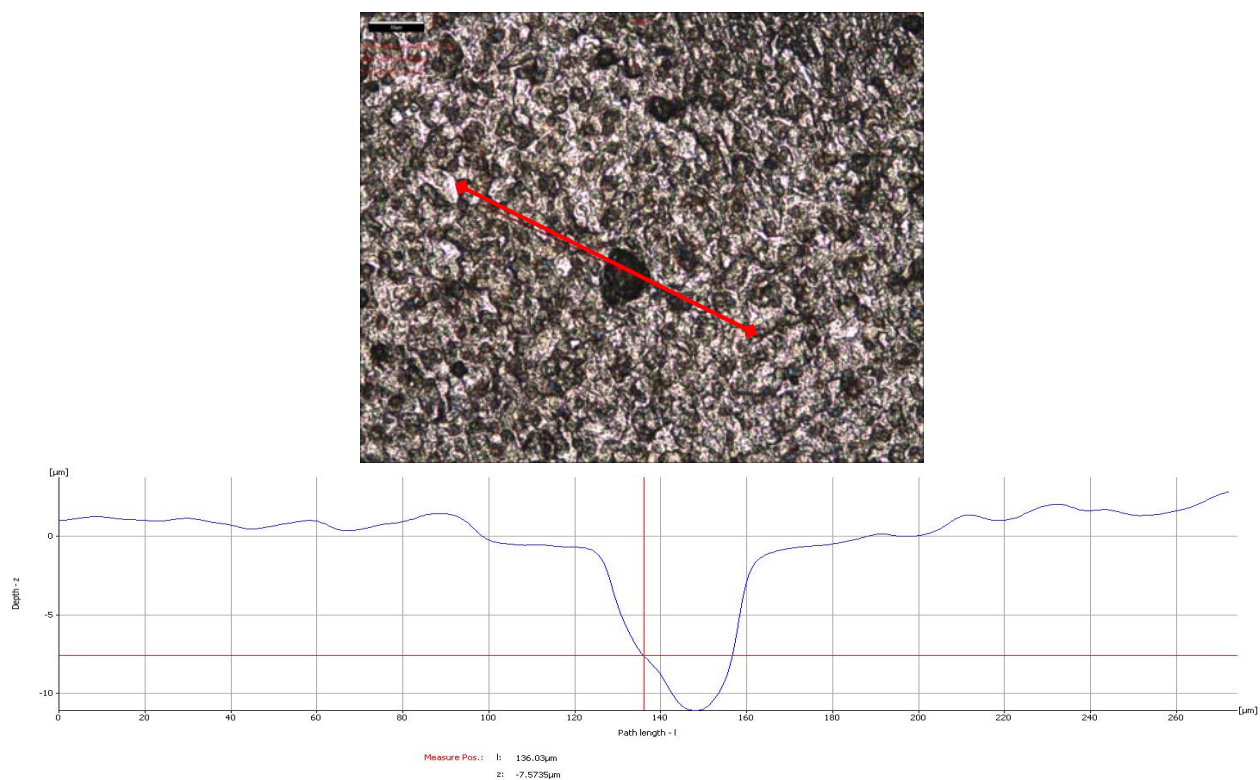


FIGURE 11 – IFM data for coupon contacted with sulfur for 1 day at 80°C, without film.

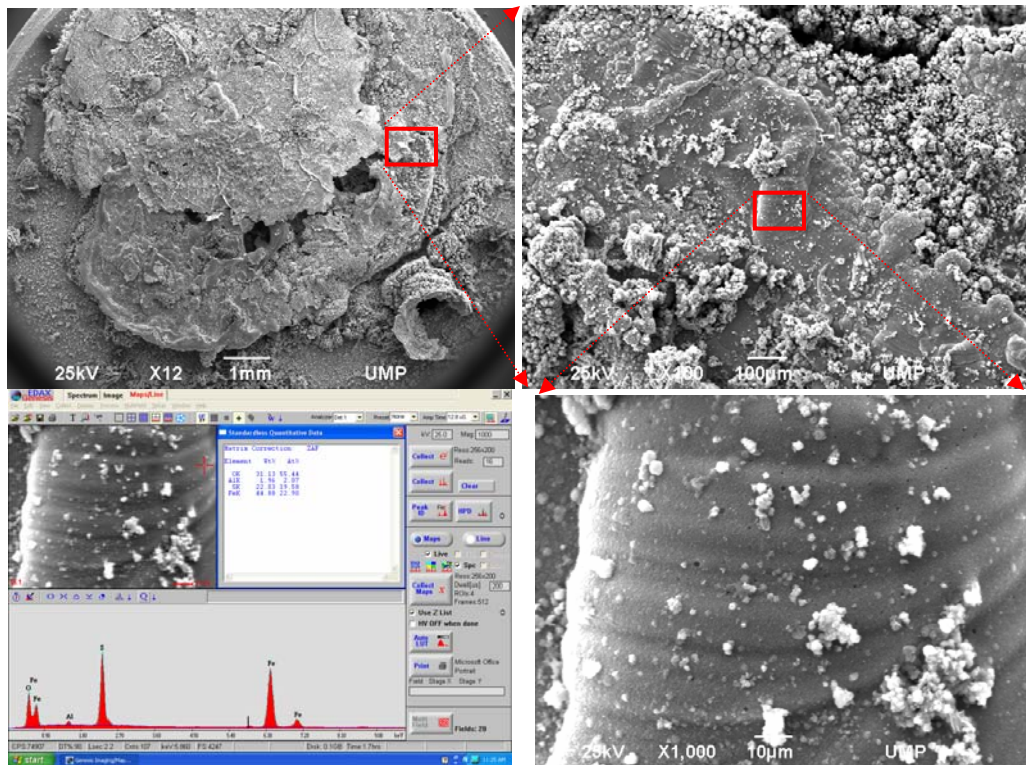


FIGURE 12 – Corrosion coupon contacted with elemental sulfur for 4 days at 80°C, with film.

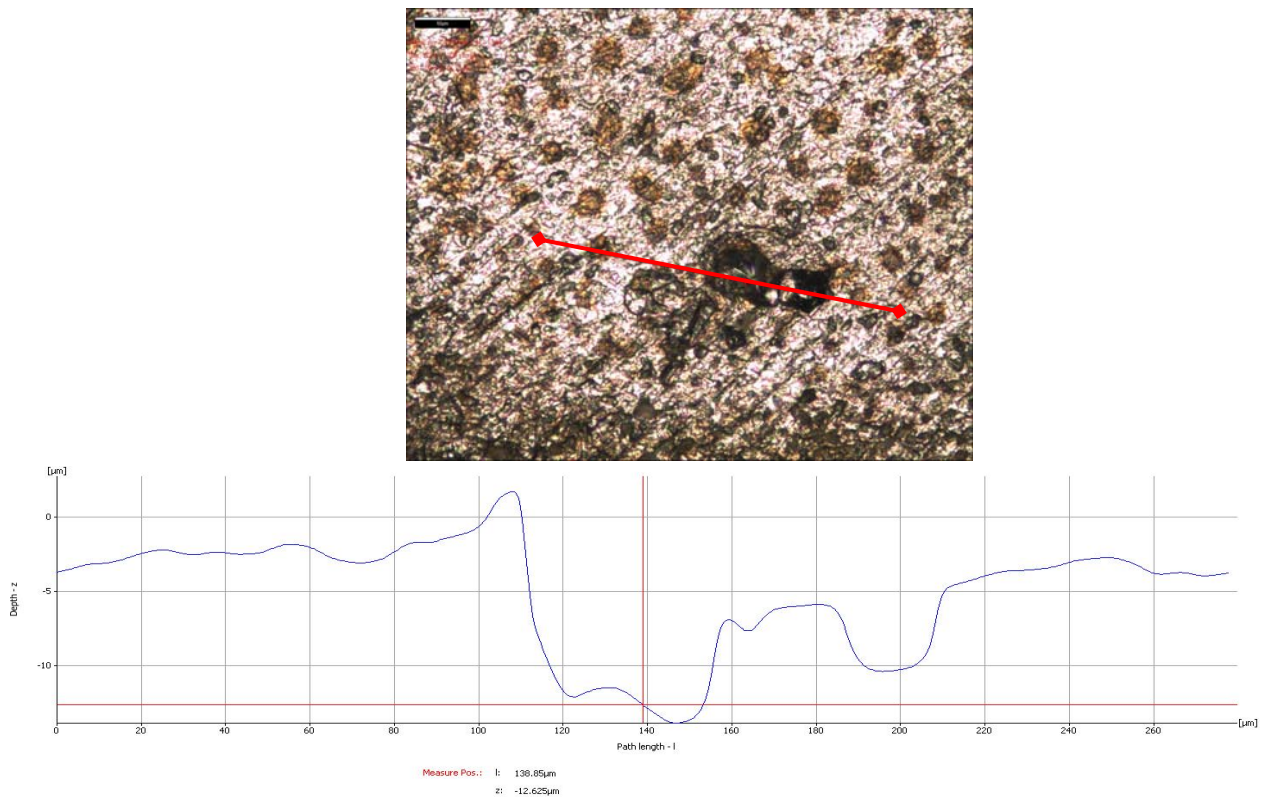


FIGURE 13 – IFM data for coupon contacted with sulfur for 4 days at 80°C, without film.

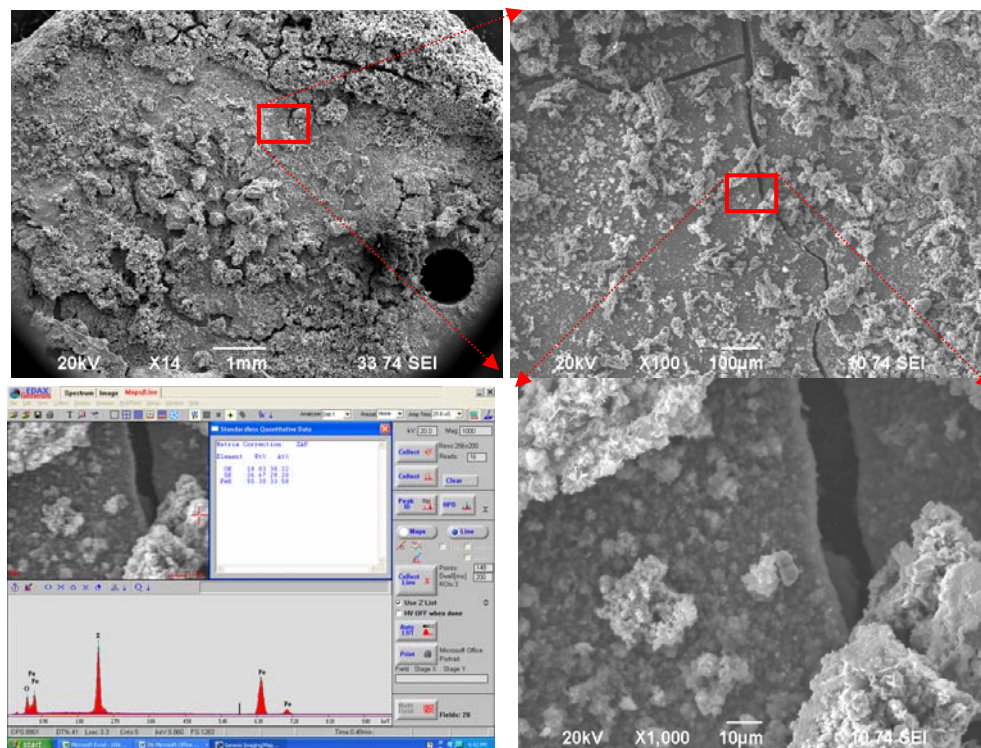


FIGURE 14 – Corrosion coupon contacted with elemental sulfur for 5 days at 80°C, with film.

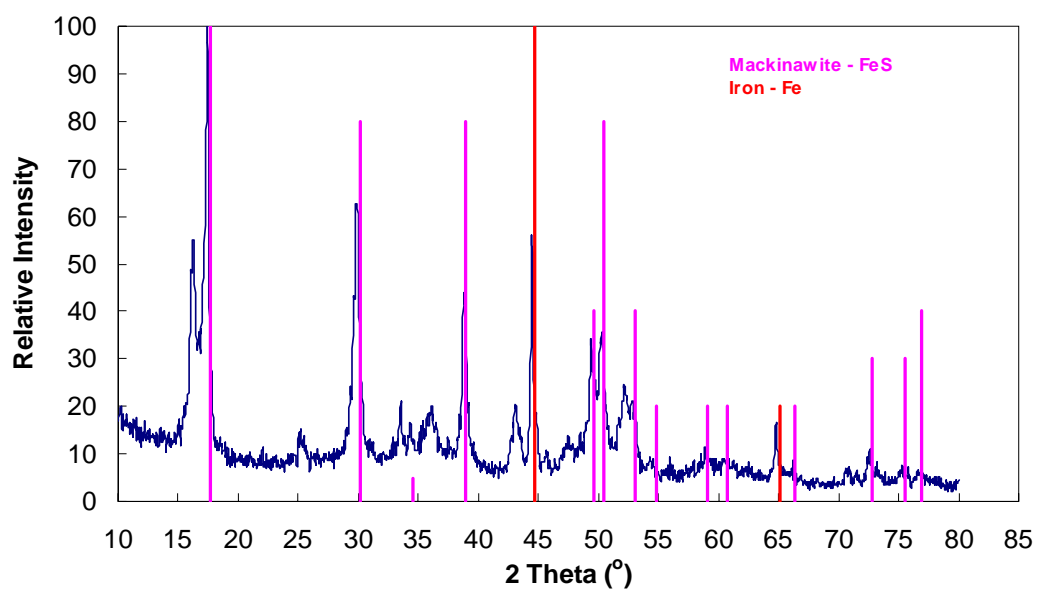


FIGURE 15 – XRD data of the corrosion product after 4 days at 80°C.

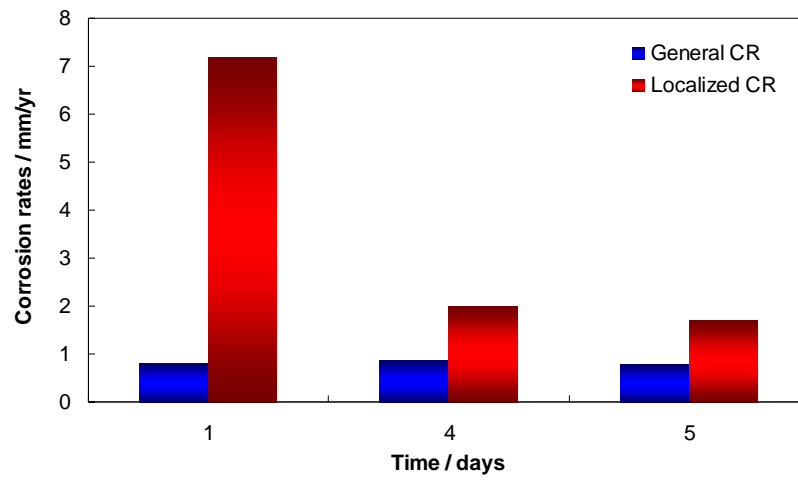


FIGURE 16 – Comparison of general and localized corrosion rates at 25°C.

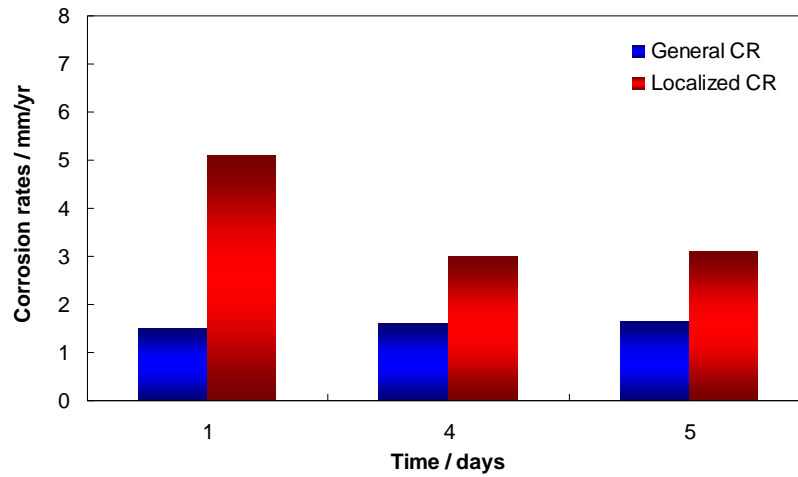


FIGURE 17 – Comparison of general and localized corrosion rates at 80°C.

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