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ELEMENTAL SULFUR CORROSION OF CARBON STEEL IN THE PRESENCE OF SULFUR SOLVENT AND MONOETHYLENE GLYCOL

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The objective of this work is to gather information about general and localized corrosion in simulated, highly sour field conditions. A series of autoclave corrosion experiments is carried out to simulate as closely as possible the conditions of a specific gas field containing high levels of H_2S and, possibly, elemental sulfur. The main three parameters of interest are the effect of elemental sulfur, sulfur solvent, monoethylene glycol (MEG) and possible mutual interactions between them. The experimental work is carried out in a 20L N10276 autoclave under 4 bars of H_2S and 10 bars of CO_2 at 40°C. Corrosion measurements were performed at the top and bottom of the line for an exposure time of 21 days. The experimental work includes weight loss calculation and characterization of the corrosion product layers. Without MEG, carbon steel samples in contact with elemental sulfur naturally experienced extensive localized corrosion attack. The addition of MEG considerably increased the extent of localized corrosion with rates measured up to 25 mm/year. A weak electrolyte and the addition of sulfur solvent mitigated, to some degree, the effect of elemental sulfur on corrosion.

Keywords: Elemental sulfur, Monoethylene glycol (MEG), Sulfur solvent

INTRODUCTION

In highly sour gas wells, elemental sulfur tends to occur due to thermochemical sulfate reduction (TSR), reduction in sulfur solubility due to temperature and pressure drop[1], H_2S decomposition, sulfate reducing bacteria (SRB) or oxygen ingress into the system. The formation of hydrogen polysulfide (H_2S_x) from the reaction of sulfur in the gas phase at high pressure and temperature could also contribute to the transportation and deposition of elemental sulfur in gas pipeline systems. Due to pressure and temperature drop, the decomposition of polysulfide occurs and leads to the formation of solid elemental sulfur and H_2S.[2] The chemical equation for this process, for a hypothetical polysulfide (H_2S_9), is shown in equation 1.
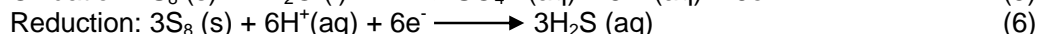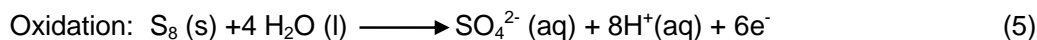
$$H_2S_9\,(g) \; \rightarrow \; S_8\,(s) + H_2S\,(g) \tag{1}$$

In the reservoir, thermochemical sulfate reduction (TSR) can happen at elevated temperatures where solid $CaSO_4$ reacts with hydrocarbon as shown in equation 2. Sulfate is then reduced from solid $CaSO_4$ by reaction with generated H_2S gas to form elemental sulfur, as shown in equation 3.

$$CH_4 + CaSO_4 \rightarrow H_2S + CO_2 + Ca(OH)_2 \tag{2}$$
$$2CaSO_4 + 6H_2S \leftrightarrow S_8 + 4H_2O + 2Ca(OH)_2 \tag{3}$$
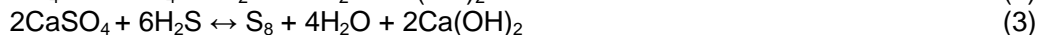
As fluid temperature and pressure change along the pipeline, conditions for saturation with elemental sulfur can also be reached.[3] On the other hand, elemental sulfur could also be formed in the presence of sulfate reducing bacteria (SRB) in the crude oil.[4] SRB will reduce SO_4^{2-} to form elemental sulfur and H_2S gas as shown in equation 4.

$$SO_4^{2-} \xrightarrow[Bacteria]{} S \longrightarrow H_2S \tag{4}$$

Accumulation of sulfur can block the production tubing and bring about catastrophic corrosion problems, especially when in contact with water.[1] Thus, research has been conducted since the 1970s to study the mechanisms of elemental sulfur corrosion, in order to create a better understanding of the process .[6,7,8] According to Maldonado-Zagal and Boden, the main corrosion mechanism relating to the presence of elemental sulfur is governed by the formation of acid due to sulfur hydrolysis, as shown in equations 5 and 6. The formation of sulfuric acid would reduce the pH of the solution, thus increasing the corrosion rate .[6]

$$\text{Oxidation: } S_8 \text{ (s) } + 4 H_2O \text{ (l) } \longrightarrow SO_4^{2-} \text{ (aq) } + 8H^+\text{(aq) } + 6e^- \tag{5}$$
$$\text{Reduction: } 3S_8 \text{ (s) } + 6H^+\text{(aq) } + 6e^- \longrightarrow 3H_2S \text{ (aq) } \tag{6}$$

However, as reported by McDonald, *et al.*, the electrochemical reaction between iron and polysulfide, as shown in equation (7), is considered to be the main mechanism controlling elemental sulfur corrosion.[7,8]

$$(x-1)Fe + S_{y-1}.S^{2-} + 2H^+ \longrightarrow (x-1)FeS + H_2S + S_{y-x} \tag{7}$$
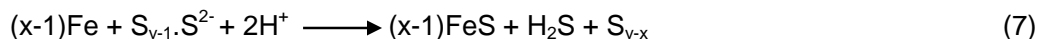
Work done by Fang *et al.* showed that the sulfur/iron electrochemical reactions play a crucial role instead of sulfur hydrolysis.[3] The presence of elemental sulfur would lead to catastrophic localized corrosion when in direct contact with the steel in the presence of electrolyte.[5] Solution acidification reported by Maldonado-Zagal and Boden was unobserved by Fang.

Various methods have been implemented to mitigate elemental sulfur corrosion in wet sour gas pipelines. As mentioned earlier, accumulation of elemental sulfur deposits can decrease or block the flow of hydrocarbons. Typically, injection of sulfur solvent is used to physically dissolve the sulfur and mitigate this issue.

Another major concern for the oil & gas industry, albeit unrelated to sulfur corrosion, is the formation of hydrates in wet gas pipelines. This issue can not only cause blockage of pipelines but also influence various types of internal corrosion processes through physical and chemical interactions (change in solubility of solid deposits, erosion of protective layers, etc.).[9] Hydrate preventers such as monoethylene glycol are widely used in wet gas pipelines to mitigate the formation of hydrates and are also known to provide some level of protection against corrosion in sweet and sour gas systems.[10,11] The presence of the hydrates preventer changes water/glycol solution properties, such as reducing the polarity of the solvent, increasing the solution viscosity and decreasing the water activity. Most of these effects tend to reduce the general corrosion rate.[12, 13] The work done by Kvarekval *et al.* showed that the presence of glycol in water solution in sour gas environments will initiate localized corrosion[12,14] although, until now, there is no mechanism to explain this interaction.

In this work, three main parameters are studied: effect of elemental sulfur, sulfur solvent and monoethylene glycol on corrosion at the top and bottom of the line. In addition, possible synergistic effects are also investigated.

EXPERIMENTAL PROCEDURE

Experiments were conducted in a 10 inch (25.4 cm) ID autoclave made of solid UNS[(1)] N10276. Steel samples were made of UNS K03014 carbon steel. A picture of the autoclave is shown in Figure 1. The design of the sample holder setup for top and bottom of the line corrosion studies is shown in Figure 2 and Figure 3. Small pellets containing approximately 1 g of elemental sulfur were deposited adjacent to the steel surface at the beginning of each test.
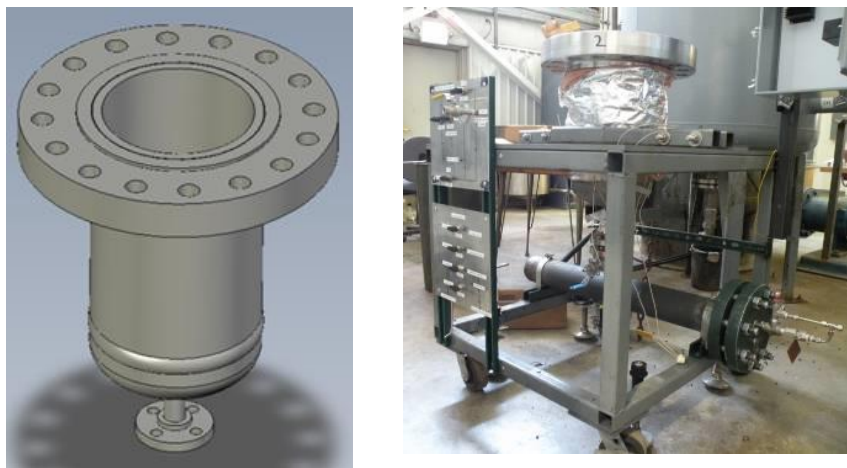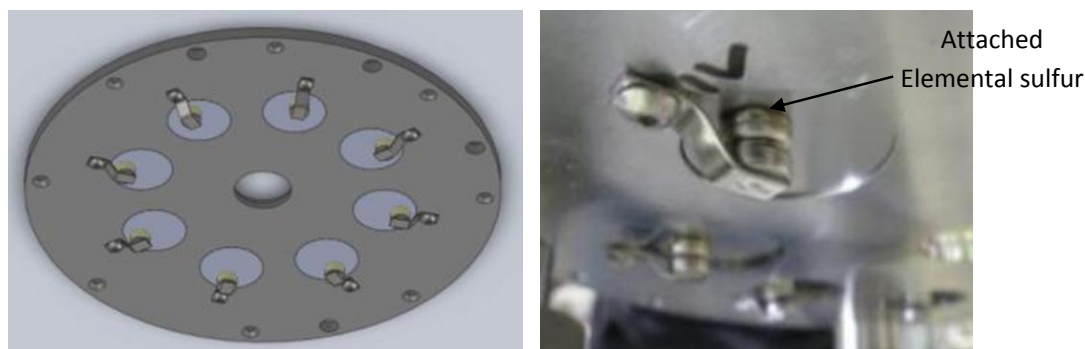

Figure 1: 20L N10276 autoclave

Figure 2: a) Sample holder setup for top of the line b) Elemental sulfur in contact with steel surface

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Figure 3: a) Sample holder setup for bottom of the line b) Elemental sulfur in contact with the steel surface

Prior to each experiment, thirteen UNS K03014 carbon steel coupons were prepared, with five selected for bottom of the line locations while the remaining eight were used for top of the line study. All of the samples were polished with 150, 400 and 600 grit sand paper, rinsed with isopropanol and air dried. The mass of the samples was recorded before the experiments were started.

The liquid compositions were varied for each of the test conditions according to Table 1. These test conditions were selected in consultation with the sponsor in order to match the field environment as closely as possible. All of the tests were performed at 4 bars of H_2S and 10 bars of CO_2 with a total pressure of 25 bars. In Test 1, the effect of elemental sulfur alone on corrosion of carbon steel was studied. This test was followed by an experiment investigating the effect of sulfur solvent in dissolving elemental sulfur. The influence of MEG in the presence of elemental sulfur and sulfur solvent was then investigated. The sulfur solvent was a mixture of straight and branched paraffins, ranging from $C_{12}H_{26}$ to $C_{17}H_{36,}$ with the aromatics isopropyl benzene (C_9H_{12}), and methylnaphtalene ($C_{11}H_{10}$). A key benefit of making such a hydrocarbon mixture in-house is that reproducibility can be guaranteed between solvent batches.

For bottom of the line conditions, the steel samples were positioned at three different levels as shown in Figure 4 for Tests 2 and 3. Two samples, one with and one without elemental sulfur, were placed in the aqueous solution, followed by another two at the interface between the sulfur solvent and aqueous solution. A final sample with elemental sulfur was placed in the sulfur solvent region. For the top location, four samples with elemental sulfur and four without elemental sulfur were also included for all tests.

The samples were taken out after 21 days of exposure for analysis. The procedure involved weight loss analysis following the ASTM[2] G1-03[15], cross-section and surface characterization using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), measurement of pit depth by profilometry, and X-ray diffraction (XRD). However, in an effort to limit the length of the paper and maintain the clarity of the main findings, only the results for weight loss and profilometry analysis are shown and discussed.

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[2] American Society for Testing and Materials (ASTM). West Conshohocken, PA 19428-2959, USA
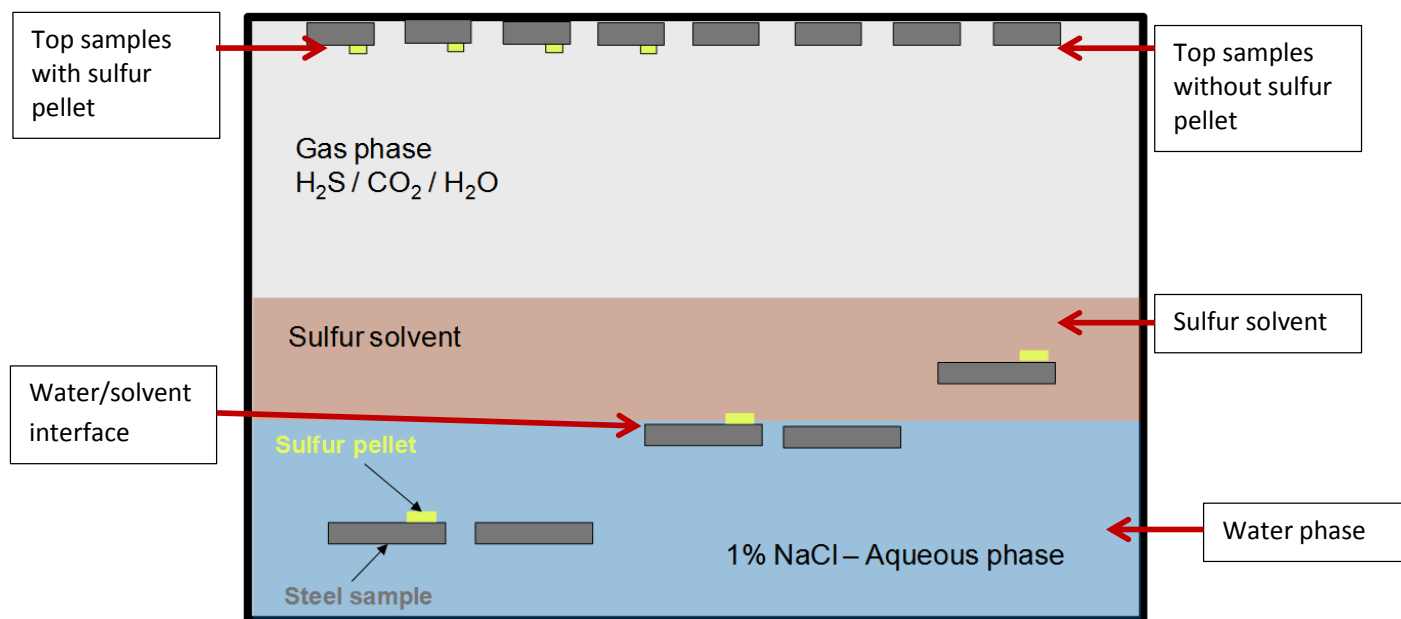
Figure 4: Schematic representing the samples position for Test 2 and 3

Table 1: Test matrix

Parameters	Test 1	Test 2	Test 3
Investigating	Elemental sulfur	Elemental sulfur & sulfur solvent	Elemental sulfur, sulfur solvent & MEG
Liquid phase composition (bottom of the line)	1 wt.% NaCl	1 wt% NaCl (86.6 vol%) & sulfur solvent(13.4 vol %)	1 wt% NaCl (46.4vol%), sulfur solvent(13.4 vol %) & MEG(40.2 vol %)
Test material	UNS K03014 carbon steel		
Gas temperature (˚C)	40		
Top sample temperature (˚C)	20		
Water condensation rate for top samples (ml/m^2/s)	0.05		
Total pressure (bar)	25		
CO_2 partial pressure (bar)	10		
H_2S partial pressure (bar)	4		
Elemental sulfur content (g)	1*		
Undissociated acetic Acid (ppm)	350		
Test duration (days)	21		

: 1 g pellet of elemental sulfur (powder) is deposited on the surface of the steel at the beginning of each test

RESULTS AND DISCUSSION

Top of the line samples

Comparisons of general and localized corrosion rates for top of the line samples are shown in Figure 5. In all cases, the top samples were mostly uniformly corroded and only isolated pitting, measured at up to 2.5 mm/year, could be observed. No clear correlation between the location of the pitting and the elemental sulfur pellet could be made. The low conductivity of the condensed water could explain why no extensive pitting was identified on the top samples. The presence of the sulfur solvent at the bottom of the line did not seem to have a clear effect on TLC rates (general or localized) as the sulfur pellet did not dissolve. It could be surmised that the presence of MEG or sulfur solvent had only a marginal effect on TLC rates, probably due to the low volatility of these two chemical substances. Consequently, in this paper, further discussions focus mainly on bottom of the line corrosion results.
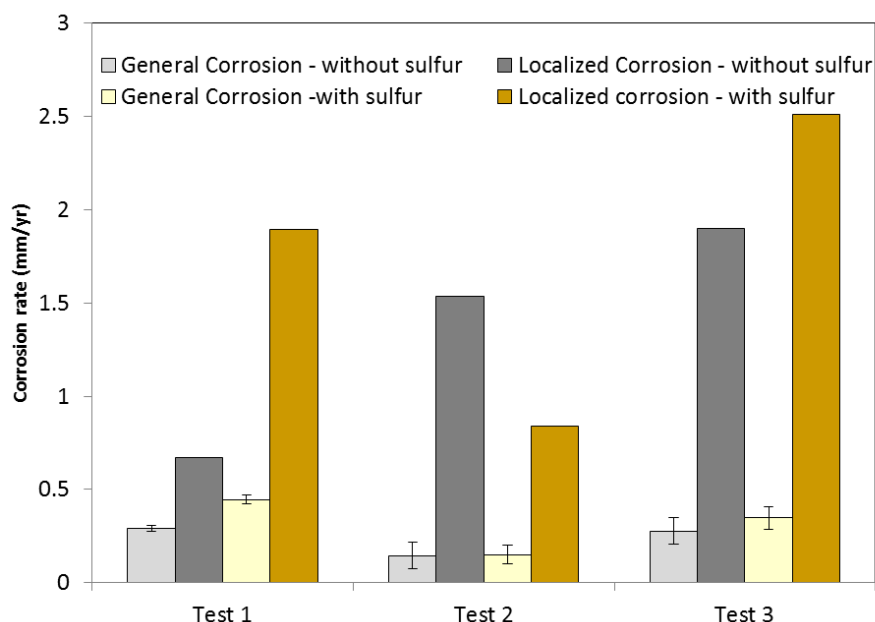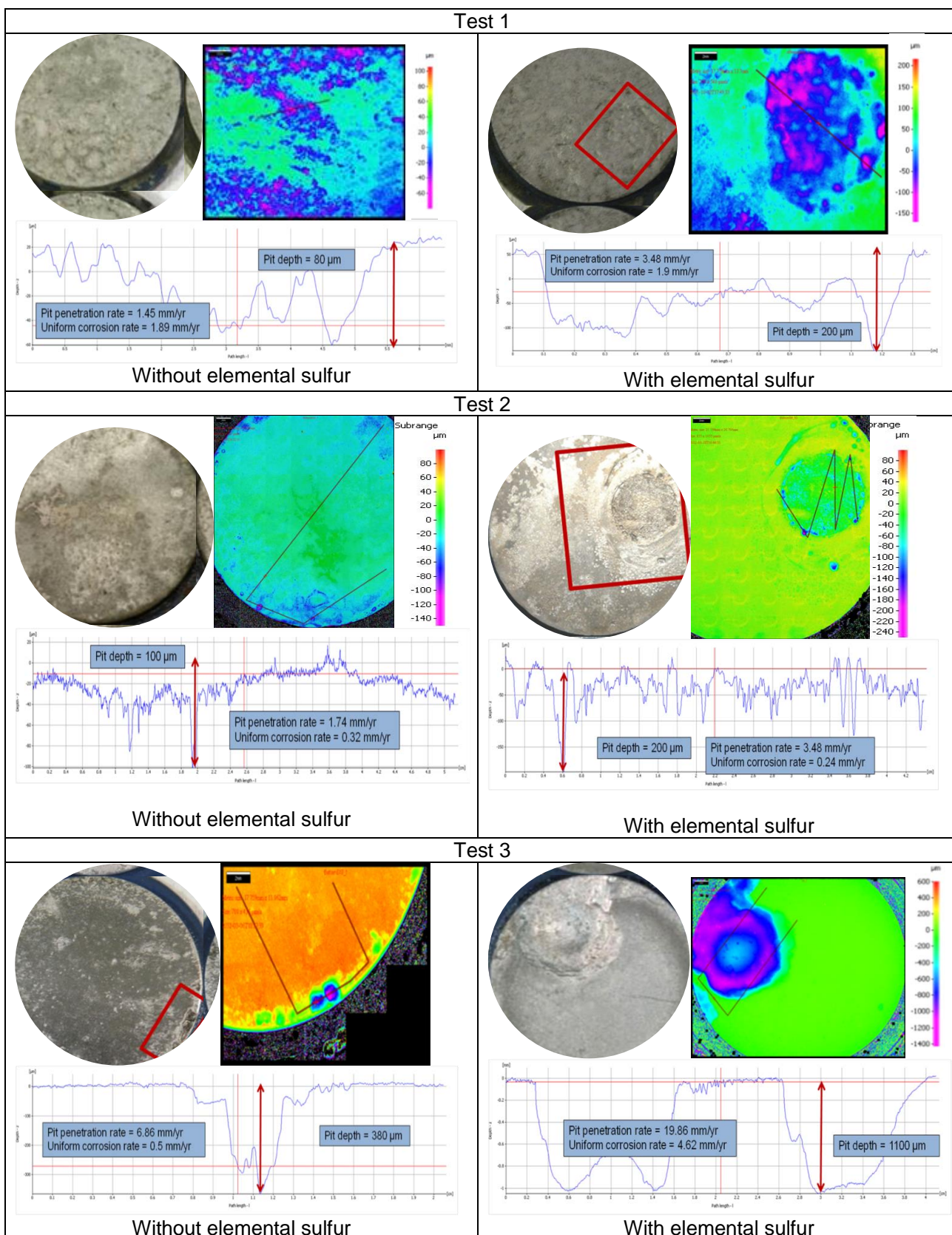

Figure 5: General and localized corrosion for top samples for Test 1, 2 and 3

Bottom samples in water phase

Surface analysis (profilometry)

The following section describes data obtained through profilometry for samples in the water phase. In Test 1, no localized corrosion was observed for samples without elemental sulfur. However, the presence of elemental sulfur on the surface of the steel led to extensive pitting, with pit penetration rates up to 3.5 mm/yr, and where pits as deep as 200 μm were found underneath the sulfur pellet. In Test 2, no significant difference in terms of pit depth was observed, as compared to the result in Test 1. This is due to the fact that the sulfur solvent has very limited solubility in the water phase. Pits as deep as 200 and 100 μm were found for samples with and without elemental sulfur, respectively. The most important finding in this work was observed in Test 3, where the presence of MEG in the water phase significantly accelerated the localized corrosion rate. As shown in Figure 6, pits as deep as 380 μm were found on the sample without elemental sulfur, which led to 7 mm/yr of pit penetration rate. In addition, the presence of elemental sulfur in this test led to a more severe pit penetration rate of up to 25 mm/yr. The area underneath the elemental sulfur suffered extreme corrosion, where a large pit as deep as 1.1 mm was observed.

Test 1	
Pit depth = 80 µm Pit penetration rate = 1.45 mm/yr Uniform corrosion rate = 1.89 mm/yr Without elemental sulfur	Pit penetration rate = 3.48 mm/yr Uniform corrosion rate = 1.9 mm/yr Pit depth = 200 µm With elemental sulfur
Test 2	
Pit depth = 100 µm Pit penetration rate = 1.74 mm/yr Uniform corrosion rate = 0.32 mm/yr Without elemental sulfur	Pit depth = 200 µm Pit penetration rate = 3.48 mm/yr Uniform corrosion rate = 0.24 mm/yr With elemental sulfur
Test 3	
Pit penetration rate = 6.86 mm/yr Uniform corrosion rate = 0.5 mm/yr Pit depth = 380 µm Without elemental sulfur	Pit penetration rate = 19.86 mm/yr Uniform corrosion rate = 4.62 mm/yr Pit depth = 1100 µm With elemental sulfur

**Figure 6: Comparison of profilometry analysis in water phase for Test 1, 2 and 3**

General and localized corrosion rates in water phase

Comparison of general corrosion rates from weight loss analysis and localized corrosion rates from the profilometry analysis with and without elemental sulfur are plotted as shown in Figure 7.

In Test 1, the highest localized corrosion rate was obtained at 5.5 mm/yr for the sample in direct contact with elemental sulfur. Without sulfur, the pitting rates were only marginally higher than the uniform corrosion rate. The general corrosion rates for samples with and without elemental sulfur were very similar, with rates measured at 1.91 mm/yr and 1.90 mm/yr, respectively. Consequently, pitting ratios (pitting corrosion rate / uniform corrosion rate) were always below 5, which, according to an internal procedure developed to evaluate pitting, does not constitute a clear case of localized corrosion.

In Test 2, where 13.4 vol% of sulfur solvent was added on top of the electrolyte, the general corrosion rate was 84% reduced, compared to Test 1, to 0.24 and 0.32 mm/year with and without sulfur, respectively. The reason behind this uniform corrosion rate reduction is not clear, since the sulfur solvent should have little effect of the chemistry in the water phase. Localized corrosion rates of up to 4 mm/yr were still obtained for the sample with elemental sulfur.

However, for Test 3, when 40.2 vol% of MEG was added in the system, the general corrosion rate with elemental sulfur was multiplied by a factor of 14 as compared to Test 2 and reached 4.6 mm/year. The localized corrosion rate was also increased dramatically (up to 25 mm/yr) for the sample in contact with elemental sulfur. The localized corrosion rate for bare steel was also increased to 7 mm/yr.
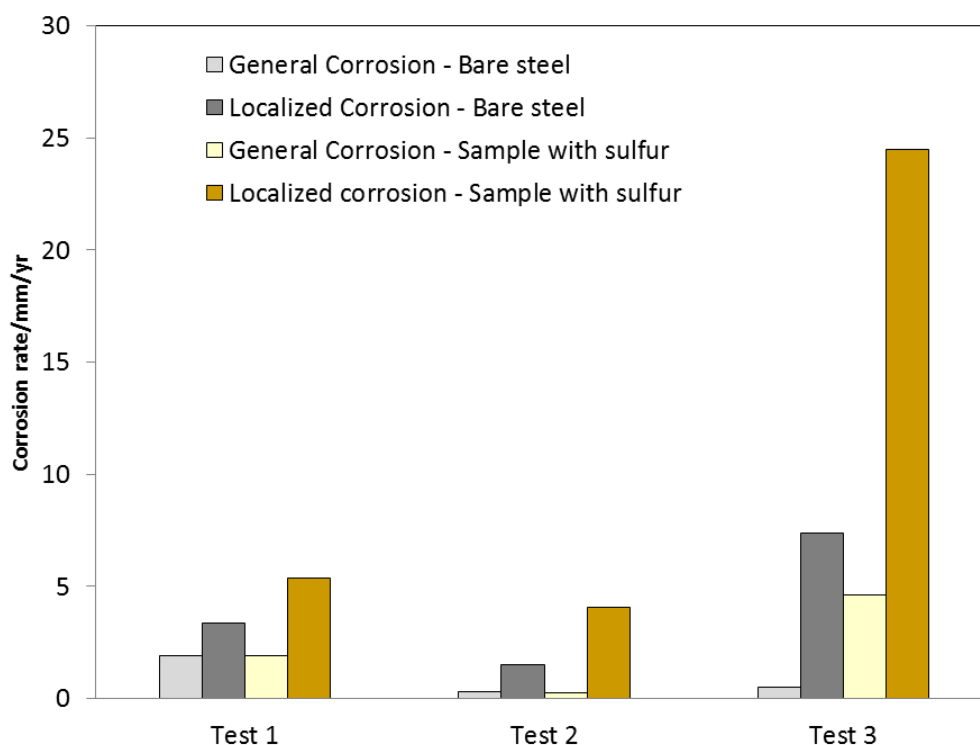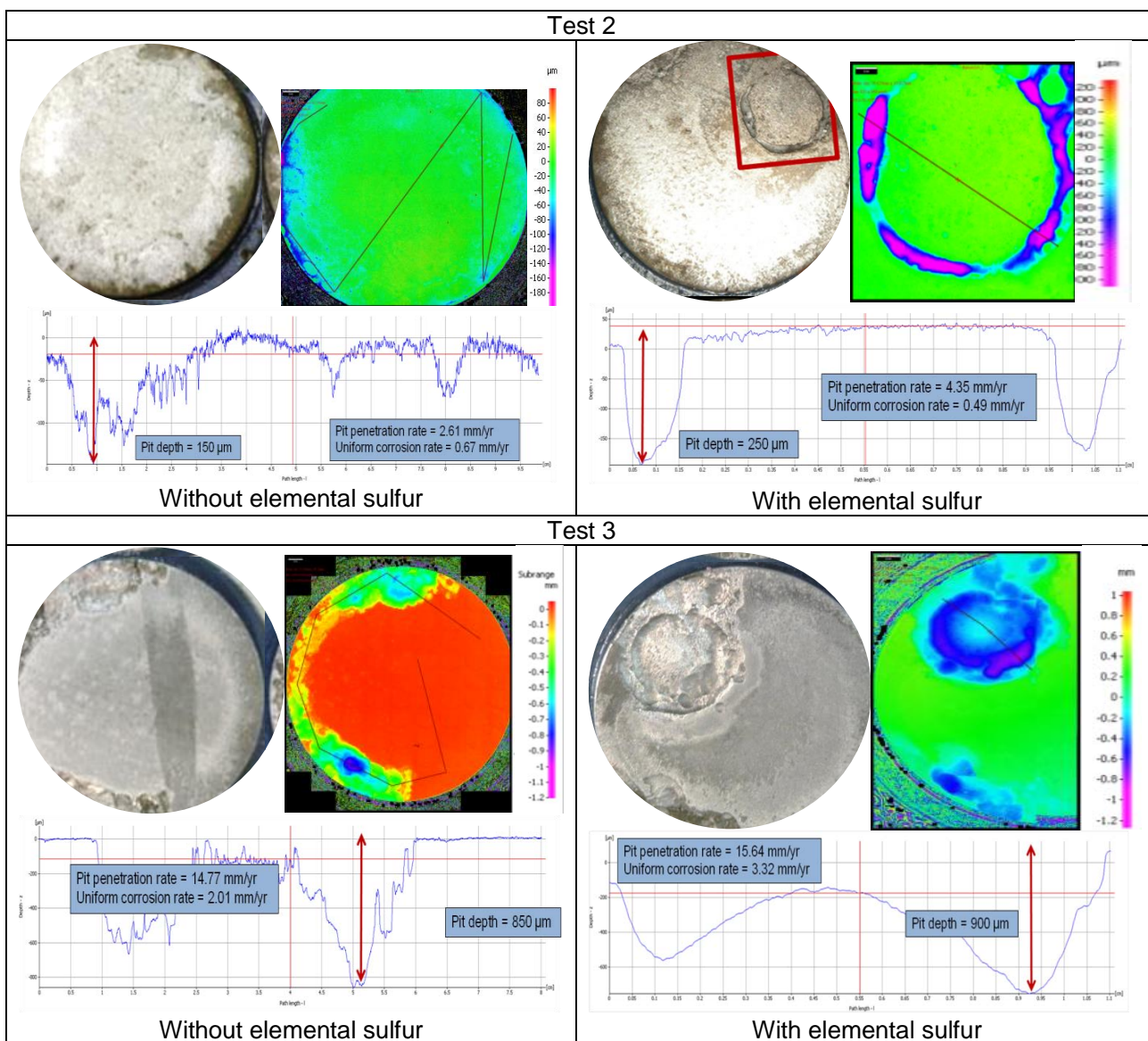

Figure 7: General and localized corrosion in the water phase for Test 1, 2 and 3

Bottom samples at water/sulfur solvent interface

Surface analysis (profilometry)

Figure 8 presents the analytical data for the samples located at the water/sulfur solvent interface. In Test 2, the surface profile analysis showed high penetration rates, but mostly on the border of the sample. Consequently, an artificial edge effect cannot be ruled out, as the center part of the sample appears to be uniformly corroded. Pit depths of 150 μm were found on the sample without elemental sulfur, which led to 2.6 mm/yr of pit penetration rate. The pit depth was increased underneath the sulfur pellet to 250 μm. The same corrosion behavior observed in the water phase in the presence of MEG was observed in Test 3. Pits as deep as 900 and 850 μm, respectively, were detected. Samples in contact with the elemental sulfur pellet suffered the most localized corrosion, especially in the presence of MEG.
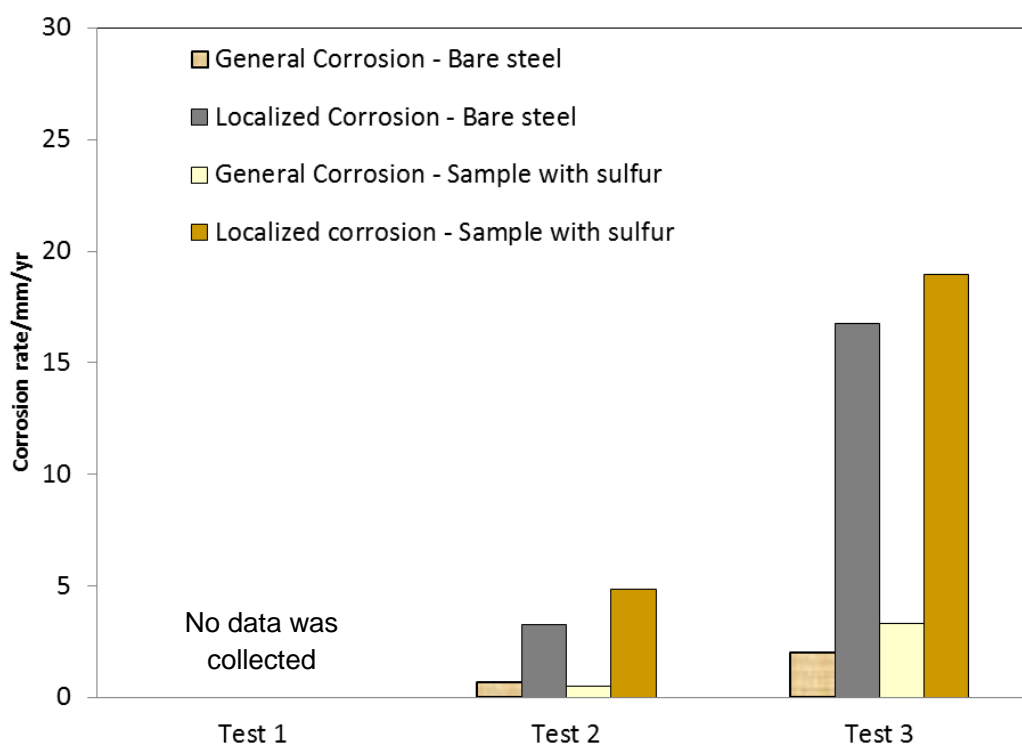

Figure 8: Comparison of profilometry analysis for water/sulfur solvent interface for Test 2 and 3

General and localized corrosion rates

General and localized corrosion rates for samples at the water/solvent interface are also compared in Figure 9. The comparisons can only be made between Test 2 and Test 3, since there were no sulfur solvents in Test 1. The presence of MEG in water increased the localized corrosion rate from 3 mm/yr to 17 mm/yr for bare steel (without elemental sulfur) and from 5 mm/yr to 19 mm/yr for sample with elemental sulfur. The effect of MEG in accelerating the localized corrosion rate could clearly be seen. It was also shown that samples with elemental sulfur for both Test 2 and 3 suffered higher localized corrosion rates as compared to samples without elemental sulfur. In addition, the location of the sulfur pellet correlates very well with the location of the most extensive localized attack.

The presence of MEG in the H_2S environment could accelerate the localized corrosion up to 25 mm/yr in the presence of elemental sulfur. However, the main mechanism behind this behavior still remains unclear. A hypothesis which could explain the acceleration of localized corrosion rate with the presence of MEG in H_2S environment is that the MEG would undergo a chemical reaction with H_2S to form thiols (R-SH). Thiol will then react with ferrous ion (Fe^{2+}) to form complexes that would impede the formation of protective FeS layer, thus accelerating the corrosion rate. However, this hypothesis has yet to be tested.
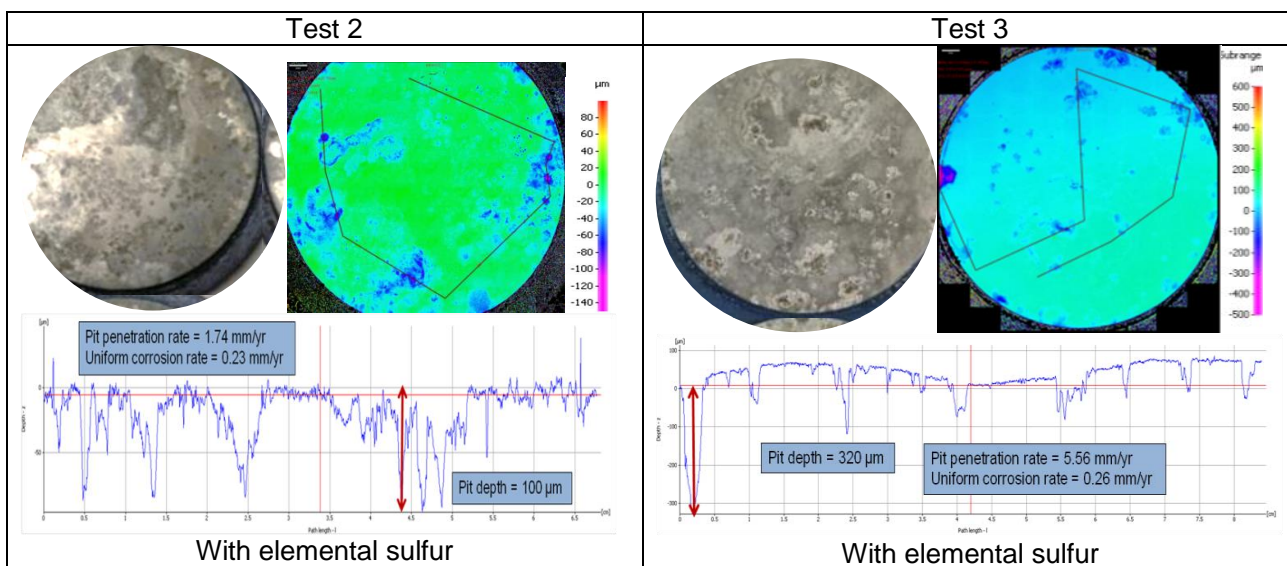

Figure 9: General and localized corrosion for water/solvent interface for Test 2 and 3

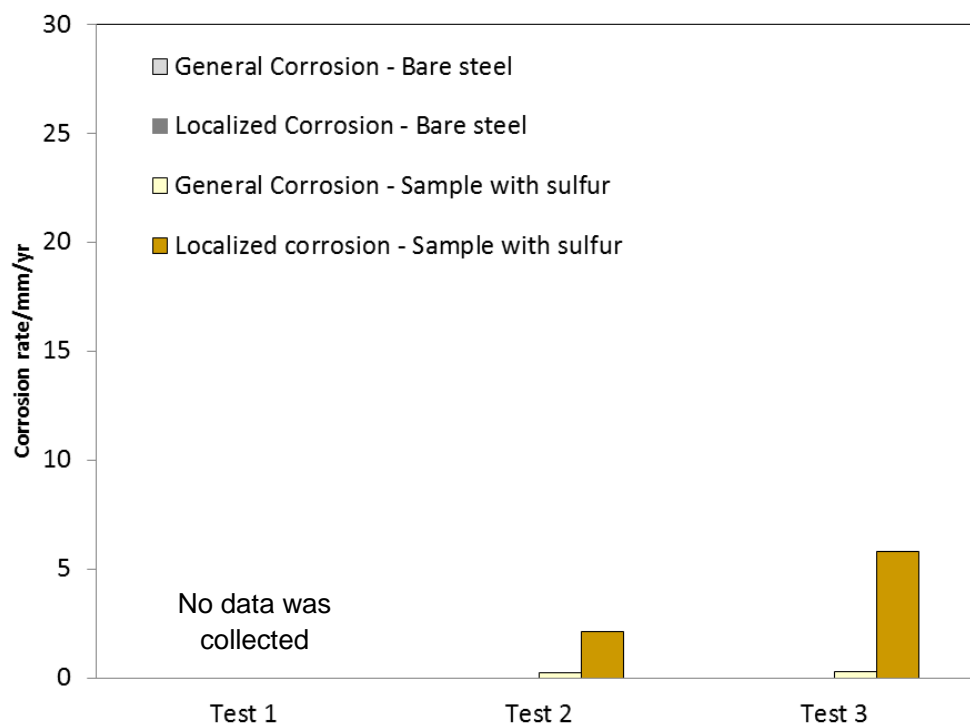**Bottom samples in sulfur solvent**

<u>Surface analysis (profilometry)</u>

In Figure 10, only one sample with elemental sulfur was placed in the sulfur solvent phase for Tests 2 and 3. Some pits as deep as 100 µm were found all over the surface in Test 2 (representing localized corrosion at 1.97 mm/yr). Pits as deep as 320 µm were found at the edge of the coupon leading to localized corrosion of 5.56 mm/yr in Test 3. Even though the entire sulfur pellet was dissolved after the test, a few pits could still be found.

Figure 10: Comparison of profilometry analysis in sulfur solvent region for Test 1, 2 and 3

<u>General and localized corrosion rates</u>

In Figure 11, only samples with elemental sulfur were placed in the sulfur solvent region for both Test 2 and 3. Compared to previous data collected in the water phase or at the interface water/solvent, relatively low general corrosion rates were obtained, with rates measured at 0.2 mm/yr. Localized corrosion rates were also significantly reduced to 2 mm/yr and 6 mm/yr in Test 2 and 3, respectively. The sulfur solvent managed to dissolve the elemental sulfur and reduce the localized corrosion rate. However, the effect of MEG could still be seen in Test 3, as the localized corrosion rate was increased up to 6 mm/yr.

Figure 11: General and localized corrosion for samples in the sulfur solvent for Test 2 and 3

CONCLUSIONS

The corrosion behavior of pipeline steels in $CO_2/H_2S/H_2O$ mixtures in the presence of elemental sulfur, sulfur solvent and MEG was investigated by weight loss measurements and surface analysis techniques. The following conclusions are drawn according to the location of the samples.

Top of the line – Vapor phase

- General corrosion rates remain relatively low in all conditions tested, as the presence of MEG or sulfur solvent at the bottom of the line did not seem to have any effect on the extent of corrosion. This is probably due to the low volatility of these chemical substances in the conditions tested.
- The presence of elemental sulfur pellet in direct contact with the steel surface did not seem to lead to localized corrosion as expected. This is probably due to the low electrical conductivity of the electrolyte (condensed water).
- Some isolated pitting was observed but no correlation could be established with the presence of elemental sulfur.

Bottom of the line - Water phase

- The presence of elemental sulfur in contact with the steel surface clearly promotes pitting, especially on areas in direct contact with or in proximity to the sulfur pellet. This statement is full agreement with the literature.
- The presence of MEG led to a dramatic increase in the general and localized corrosion rates. Localized corrosion rates were measured up to 25 mm/yr right underneath the sulfur pellet. The mechanism behind the enhanced corrosion in the presence of MEG is not known as of now. The formation of thiols that could impede the formation of protective iron sulfide layers is hypothesized.

Bottom of the line - Water/sulfur solvent interface

- In general, steel samples experienced similar levels of corrosion as described for the samples in the water phase. No significant corrosion mitigation was observed due to the location of the samples at the interface water/sulfur solvent.

Bottom of the line - Sulfur solvent phase

- As expected, the sulfur solvent did dissolve the entire elemental sulfur pellet, as no trace of sulfur was found after the test on the steel surface.
- Even though the sulfur was fully dissolved, random isolated pitting was still observed in several areas of the samples.
- The highest localized corrosion up to 6 mm/yr was measured when MEG was added to the aqueous solution.
- Relatively low general corrosion rates (< 0.3 mm/yr) were recorded, showing that the addition of sulfur solvent did succeed in mitigating the extent of corrosion.

ACKNOWLEDGEMENTS

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