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Sour top of line corrosion testing with methanol

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ABSTRACT

Although relatively few failures associated with sour top of line corrosion (TLC) have been reported in field, it has been recognised as a corrosion threat, particularly if methanol is present. The toxicity and flammability of H_2S, however, puts significant health, safety and environmental (HSE) restrictions on test equipment for sour corrosion testing, especially at high H_2S pressures. In this work, a specially made sample holder that can be fitted inside regular autoclaves was used for simulating sour TLC in the presence of methanol. The experiments showed that for 10 bar H_2S + 10 bar CO_2, the TLC mass loss rate was 0.2-0.3 mm/y of general corrosion without localized attacks. The presence of methanol (50% by weight in the bulk liquid phase) resulted in significant localized corrosion attacks with just a slight increase of the mass loss corrosion rate.

Key words: Top of line corrosion, H_2S, methanol, test equipment

INTRODUCTION

Top of line corrosion (TLC) has been recognized as a corrosion threat since the 1980ies.[1-11] Although the first reported cases of TLC were for sour conditions (CO_2 + H_2S),[12-14] the major focus has been on sweet TLC (CO_2 only). The number of sour TLC failures is limited compared to sweet TLC, indicating that sour TLC is a less common problem. Consequently, sour TLC has been given relatively little attention. However, several sour TLC failures in the field have been documented,[12-28] and lately more research has been carried out on this topic.[2,8,27-40]

In contrast to sweet TLC, the condensation rate is less important for sour TLC.[1] For sour TLC the steel surface temperature is important, and recent literature suggests that steel temperatures around 20 - 30 °C are more susceptible to sour TLC than at higher temperatures.[27-29] It was assumed that this effect is related to the protectiveness of the iron sulphide, which is claimed to be better at high temperature than at low temperature. Furthermore, a recent literature review showed that methanol was present in 7 out of 10 cases of failures, suggesting that the presence of methanol can have a negative impact on sour TLC, but it is obviously not an absolute prerequisite for sour TLC to occurr.[1]

The toxicity and flammability of H_2S makes sour corrosion experiments much more difficult to carry out than sweet corrosion experiments. Particularly, flow loop TLC experiments are challenging since the amount of H_2S (gas phase, dissolved in the liquid phase) would be large and therefore pose a serious HSE risk in case of leakage. Large quantities of H_2S will also make disposal of the used gas/liquid more demanding. Small scale testing in autoclaves is therefore preferred, at least for screening purposes. However, flow effects cannot be realistically mimicked since the autoclave is without gas flow and only have natural convection.

Various methods have been applied for sour TLC testing. Most methods involve forced cooling on a coupon paced inside a closed system (autoclave or flow loop). Cylindrical "cold finger" type of test coupons (Figure 1) were used in our lab (Institute for Energy Technology, IFE) earlier.[2] Although the setup was simple, the cylindrical shape made it difficult to ensure uniform condensation rate. In addition, the condensed droplets would easier fall off than on a horizontal coupon. The curved shape made the corrosion examination more difficult compared to flat coupons. Furthermore, to simulate condensation on the top of the line the coupon should face downwards. Thus it is apparent that flat coupons (facing downwards) will have several advantages with respect to uniform condensation rate and post-exposure examination.
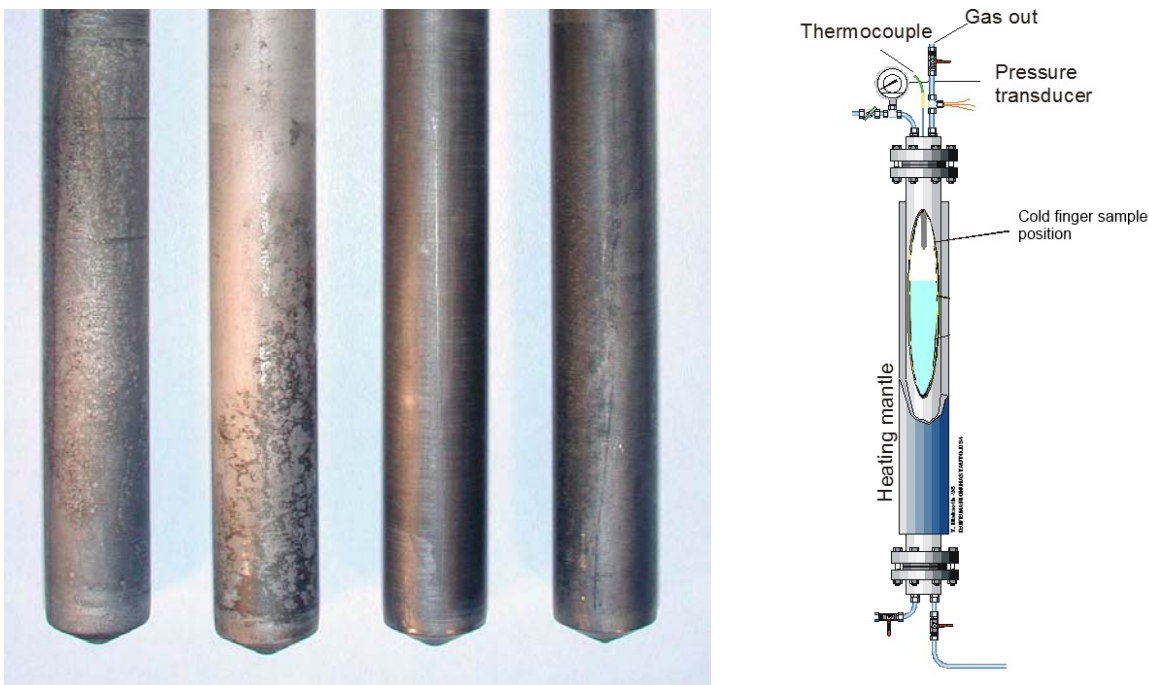

Figure 1: Cold finger coupons (left) and test-setup (right).

The present paper describes a special sample holder that is used for simulating sour TLC inside conventional autoclaves. Since it is based on a simple setup, it can probably be fitted into most types of autoclaves as long as the space requirements are fulfilled. A spray nozzle facing the TLC coupon has also been used in some experiments to mimic the effect of a spray pig with and without batch inhibitor.[2] The simple setup, limited volume (less H_2S HSE risk), and ease of operating makes it ideal for screening studies of sour TLC.

The present work was aimed at studying the effect of different condensation rates and the effect of methanol on TLC under highly sour conditions (10 bar CO_2 + 10 bar H_2S). Since the steel surface temperature is known to have an effect on sour TLC, it was kept fixed at 25°C in all experiments. The effect of different condensation rates was tested by applying different bulk temperatures. The effect of

methanol (used as a hydrate preventer in gas flow lines) was also studied by adding 50 wt.% methanol to the bulk liquid phase.

EXPERIMENTAL PROCEDURE

Corrosion coupons
The corrosion coupons were circular disks (25 mm diameter, 3 mm height) of carbon steel that were machined from cut-outs of a real pipeline. The steel composition is given in Table 1. The surface was machined to a surface finish corresponding to ~ 600 grit.

Table 1:
Steel composition (carbon steel).

C	Si	Mn	S	P	Cr	Ni	V	Mo	Cu	Al	Sn	Nb
0.06	0.26	1.05	0.001	0.01	0.02	0.26	0.048	0.01	0.01	0.029	0.003	0.047

TLC sample holder
The TLC coupon (carbon steel sample) was placed in a special sample holder of polyether ether ketone (PEEK) that exposed one side of the sample to the corrosive autoclave environment while the other (unexposed) sample side was exposed to circulating cooling liquid, as shown in Figure 2. During the experiment, the coupon was held in place by the overpressure in the autoclave. Circulation of cooling liquid was applied through a pipe-in-pipe setup, where cooling liquid inlet flow was through the inner pipe and exited through the "annulus" between the inner and outer pipe. Thus, only one pipe connection through the lid was needed. Deoxygenated mono ethylene glycol (MEG) was used as cooling liquid. Compressed air was previously used in a few experiments, but this gave less control of the coupon temperature.[2]

Bottom of line coupon
An additional corrosion coupon (same size and type as TLC coupon) was placed at the bottom of the autoclave to simulate bottom of the line (BOL) corrosion. The coupon was resting inside a PEEK holder to prevent galvanic coupling due to contact with the autoclave body.

Sample surface temperature and condensation rate
The TLC coupon surface temperature was controlled by varying the temperature of the cooling liquid. An empirical relationship (Figure 3 a) between the sample temperature, autoclave (bulk) temperature and cooling liquid was established specifically for this system using a thermocouple that was drilled into a test coupon. Coupon surface temperatures ranging from 4 °C to autoclave temperature could easily be reached. Although not used in the present experiments, it should be noted that wet-dry cycling can easily be simulated by ramping the cooling liquid above and below the autoclave temperature.

The condensation rates were measured by volumetric measurements of condensed water that was trapped in a funnel under the sample holder. The condensation area (carbon steel) was 4.9 cm², and it was assumed that condensation occurred essentially on the steel surface as PEEK has much lower thermal conductivity than steel. Measurements showed that condensation rates in the range of 0 – 1.8 g/m²s could be reached (25 – 80°C bulk temperature).

For safety reasons, the empirical temperature and condensation measurements were carried out with only nitrogen gas in the autoclave. Thus, no H_2S precautions were needed and the steel surface would remain uncorroded during the condensation measurements. However, it is believed that this did not significantly affect the steel surface temperature and condensation results.

Test procedure

Experiments were started by placing the corrosion coupon in the sample holder, filling up the test liquid (500 ml) and removing oxygen by repeated N_2 filling/evacuation cycles. When the autoclave had reached the target temperature, H_2S gas was added multiple times to reach the desired partial pressure. Subsequently, CO_2 gas was added several times to reach the desired total pressure. The cooling pump was started after the first fill with H_2S.

When the experiment was finished, the autoclave was purged with nitrogen for several hours to remove H_2S and CO_2. A special waste-system for sour gas and liquid was used to handle the purging gas and the test liquid.

When all H_2S had been removed the corrosion coupon was taken out, submerged in isopropanol to remove traces of water and then the coupon was dried in a hot oven (~50 °C).
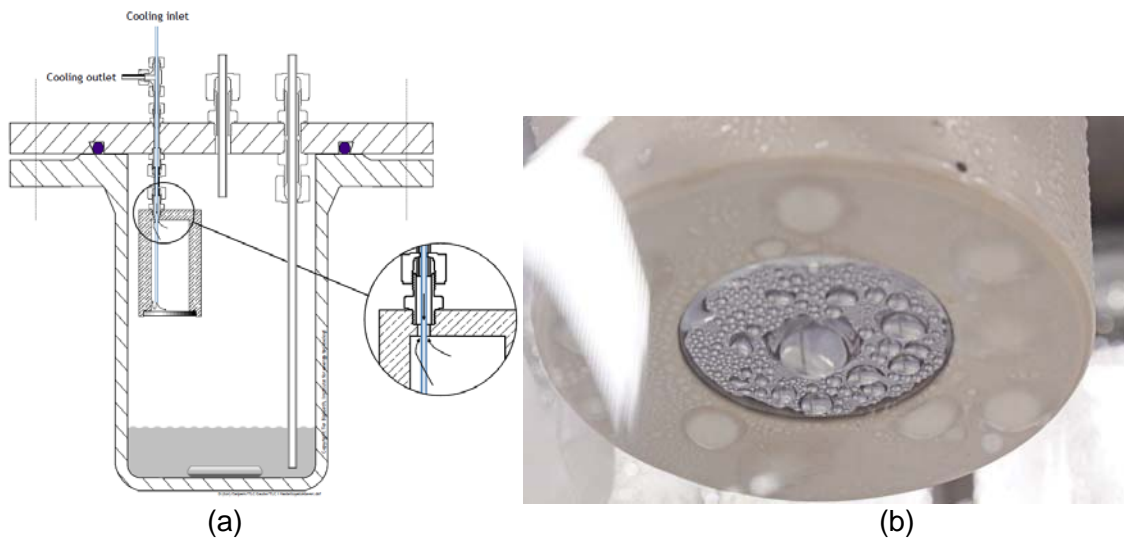

(a)   (b)

Figure 2: Schematic drawing of TLC test setup with autoclave and sample holder (a).
Picture of sample holder with corrosion coupon and condensing water (b).

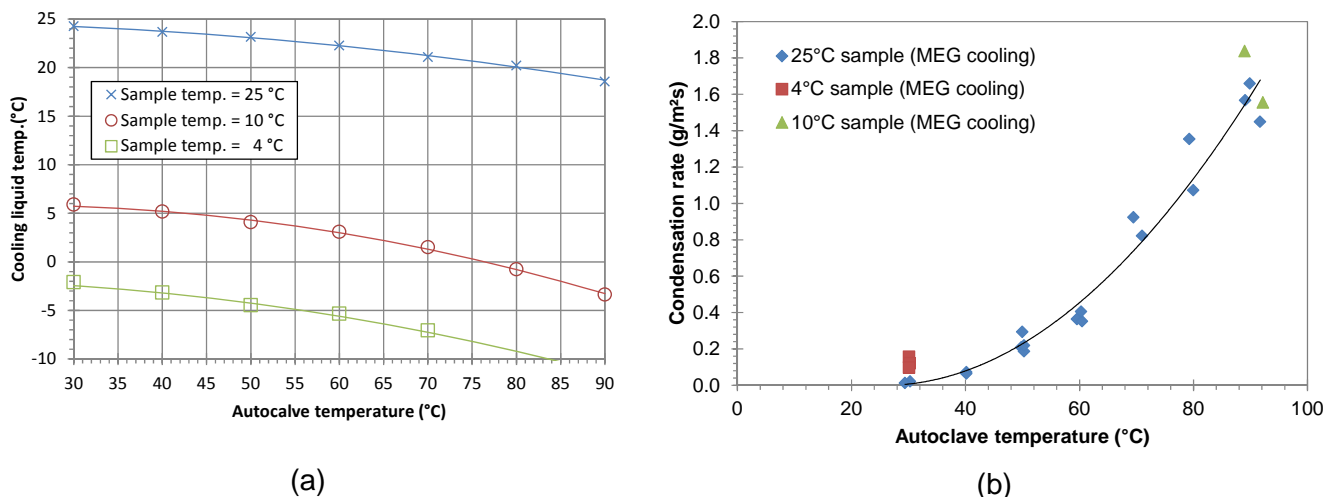(a)   (b)

Figure 3: Required temperature of the cooling liquid (MEG) as a function of autoclave temperature and sample temperature (a). Measured condensation rates as a function of autoclave temperature and sample temperature (b).

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Test conditions

Three autoclave experiments with 10 bar H_2S and 10 bar CO_2 were carried out in this work. The temperature of the corrosion coupon was fixed at 25 °C for all experiments. The two first experiments tested the effect of condensation rate by applying different bulk temperature (40 vs. 80°C) while the third experiment tested the effect of methanol. A summary of the test conditions are shown in Table 2.

Table 2: Experimental parameters.

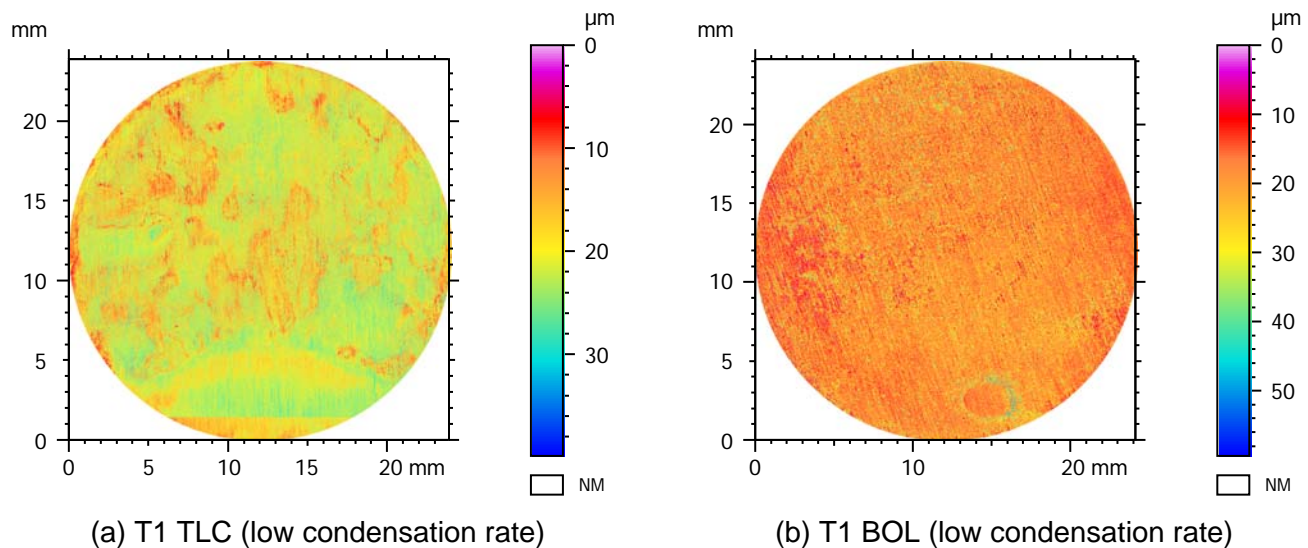| Exp. ID	TLC coupon temp. (°C)	Bulk temp. # (°C)	Cond. rate (g/m²s)	H_2S (bar)	CO_2 (bar)	NaCl (g/L)	Exp. time (days)	Liquid phase
T1	25 ± 1	40	0.079	10	10	0.1	14	Water + 0.1 g/kg NaCl
T2	25 ± 1	80	1.1	10	10	0.1	14	Water+ 0.1 g/kg NaCl
T3	25 ± 1	80	*	10	10	0.1	14	50wt.% water + 50wt.% methanol + 0.1 g/kg NaCl

\# Temperature of bulk phase (gas and liquid) inside the autoclave.

* Cond. rate were not measured for 50 wt.% methanol

RESULTS

The results from the corrosion testing are shown in Table 3. The TLC mass loss corrosion rate was 0.3 - 0.4 mm/y, and did not change much with condensation rate (i.e. bulk temperature) or with the additional presence of methanol in the bulk phase.

The TLC coupons exposed only to water vapour (T1, T2) did not have any sign of localized corrosion, but the introduction of methanol (T3) caused significant pitting and localized corrosion, as shown in the 3D images in

(a) T1 TLC (low condensation rate)

(b) T1 BOL (low condensation rate)

(c) T2 TLC (high condensation rate)

(d) T2 BOL (high condensation rate)

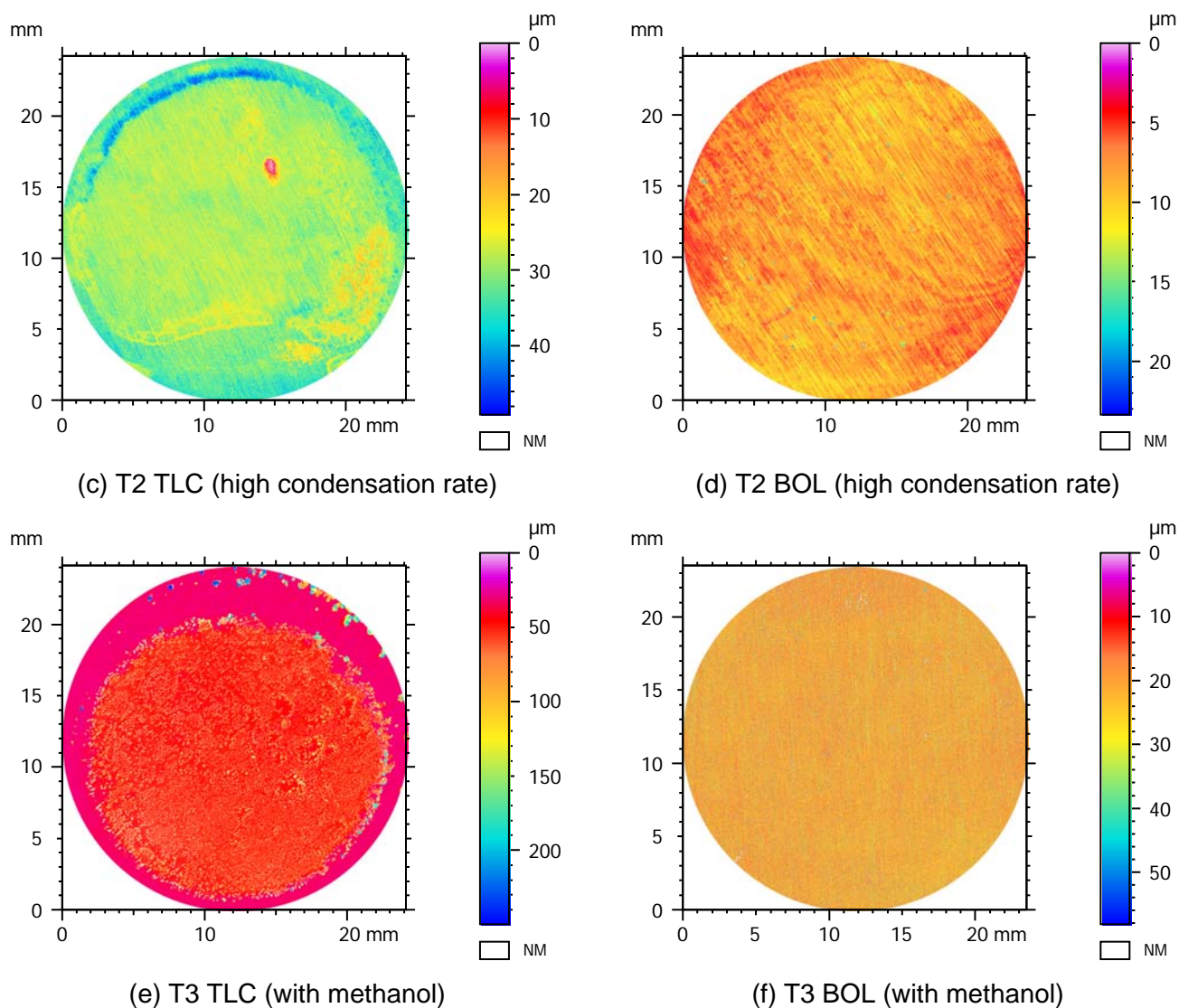(e) T3 TLC (with methanol)

(f) T3 BOL (with methanol)

Figure 4. More detailed 3D images of the methanol TLC coupon (T3) are shown in Figure 5. Localized attacks with up to 220 μm depth were present, particularly near the edges. In the central part, which had a corrosion morphology different from the edges, had general surface roughening corresponding to about 20 - 40 μm depth and in addition localized attacks (pits) with 40 - 120 μm depths. It is not known why this difference in corrosion morphology occurred with methanol, but it is probably somehow related to a liquid meniscus that formed on the edge of the coupon, between the coupon and the PEEK sample holder.

The corrosion coupons located in the liquid bulk phase (BOL) had a general mass loss corrosion rate of 0.1 – 0.4 mm/y, and only a few shallow localized attacks. In contrast to the TLC coupon exposed to methanol, the BOL coupon had very low corrosion rate (0.04 mm/y) and no localized corrosion.

Table 3: Experimental results.

Exp. ID	Sample temp. (°C)	Bulk temp. # (°C)	Corr. rate (mm/y)	Max corr. depth (μm)	Pit rate (mm/y)	Corrosion morphology
TLC coupons						
T1-TLC	25	40	0.29	20	0.52	General (uniform) corrosion.

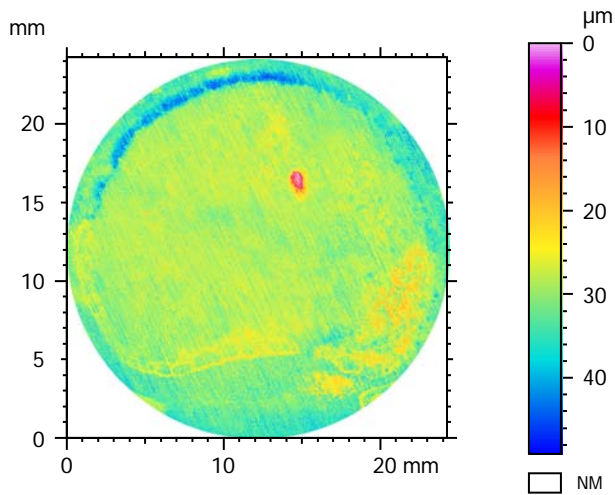|						
T2-TLC	25	80	0.25	20	0.52	General (uniform) corrosion.
T3-TLC	25	80	0.36	220	5.7	Localized and general (uniform) corrosion.
BOL coupons						
T1-BOL	40	40	0.38	40	1.0	General (uniform) and localized corrosion.
T2-BOL	80	80	0.12	30	0.77	General (uniform) corrosion.
T3-BOL	80	80	0.04	55	1.4	General (uniform) corrosion.

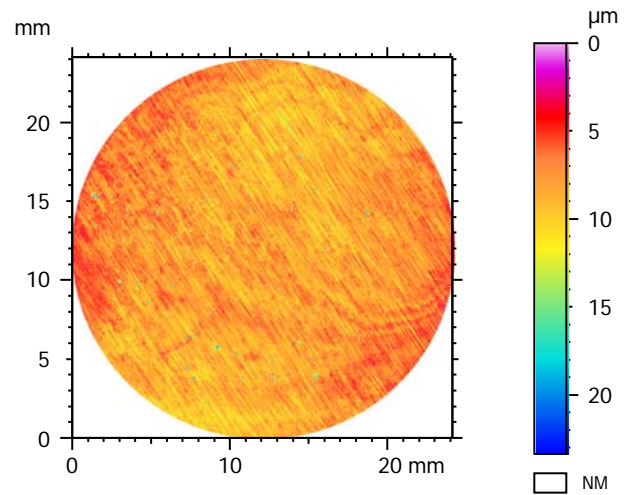\# Temperature of gas and liquid phase inside the autoclave.
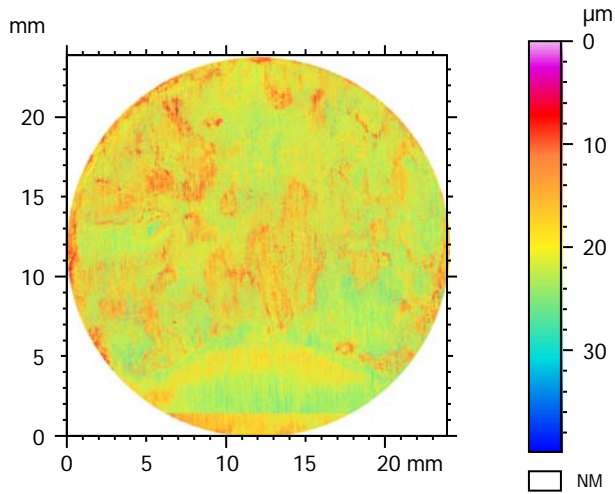
(a) T1 TLC (low condensation rate)
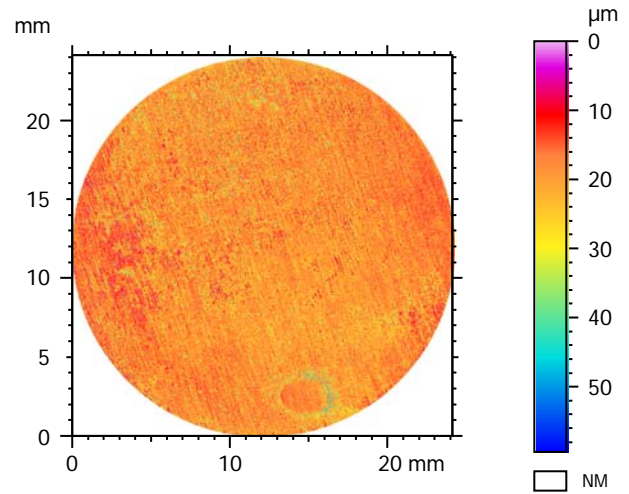
(b) T1 BOL (low condensation rate)

(c) T2 TLC (high condensation rate)
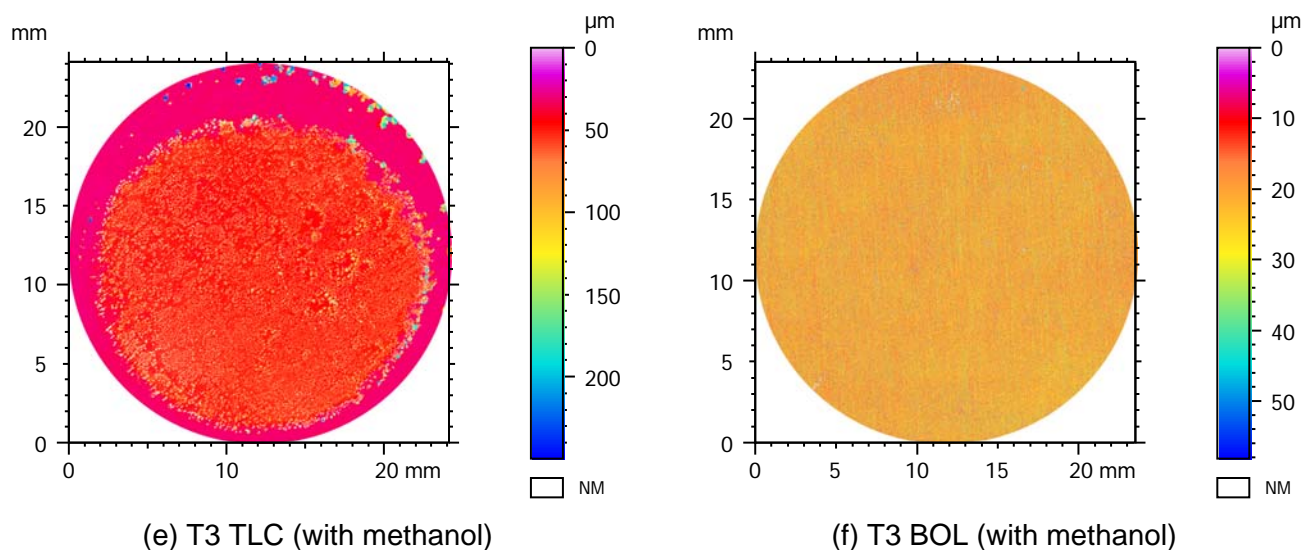

(d) T2 BOL (high condensation rate)

(e) T3 TLC (with methanol)

(f) T3 BOL (with methanol)

Figure 4: 3D images of exposed corrosion coupons.

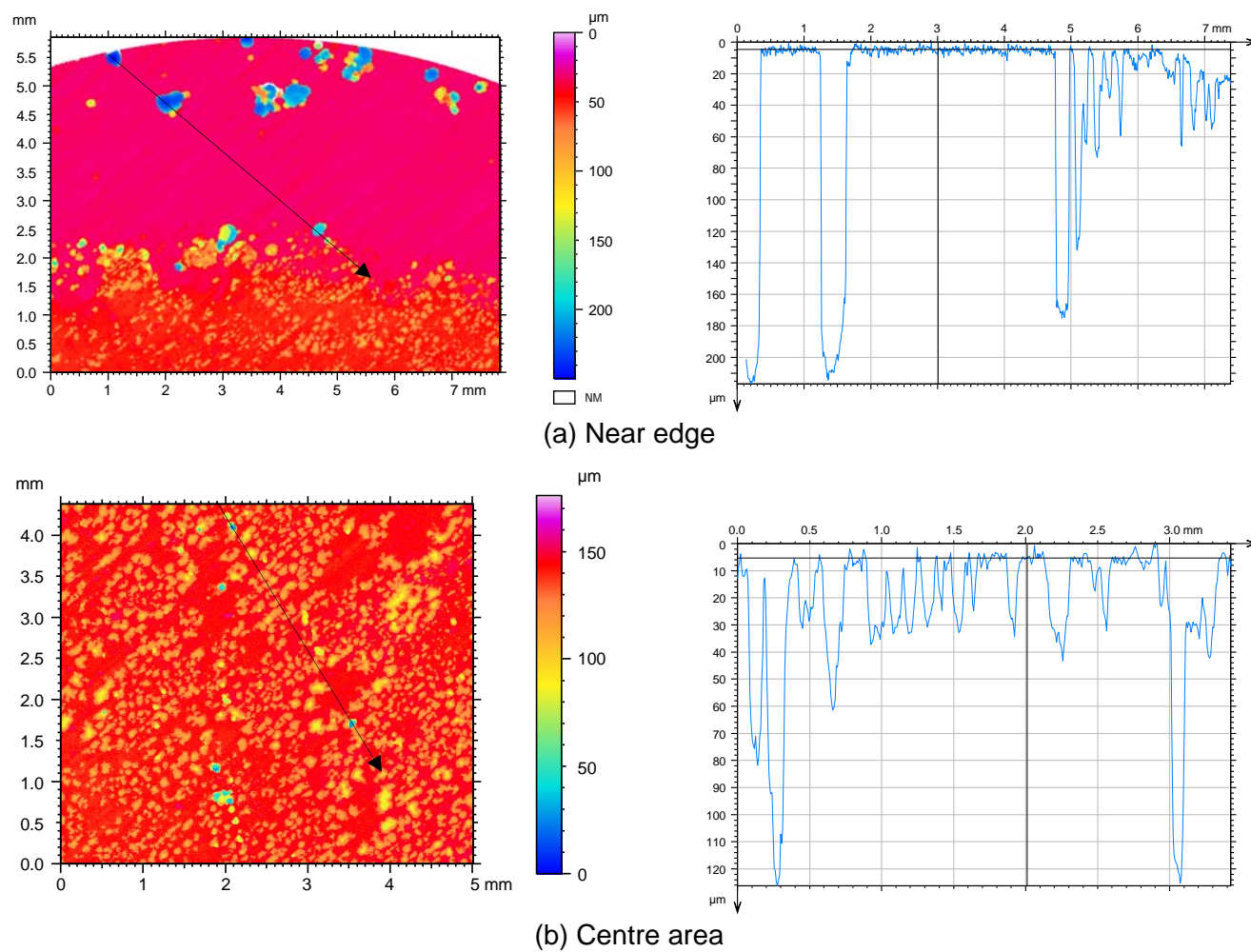(a) Near edge

(b) Centre area

Figure 5: 3D images and height profiles of T3 TLC coupon exposed to methanol. The black arrows indicate the path of the height profile.

DISCUSSION

The present results demonstrated clearly the detrimental effects of methanol on sour TLC. Methanol caused significant localized attacks, both with respect to attack depth but also with respect to attack density. The general (mass loss) corrosion was just slightly increased with methanol, but areas with increased general corrosion rate (surface roughening) were clearly visible. This is in agreement with most findings in the literature, reporting enhanced sour TLC with use of methanol.[1] Several authors reported that they suspected oxygen ingress due to insufficient deoxygenation of the injected methanol, and thus it was believed that the problem was more or less related to oxygen ingress.[18,24] The present experiments have shown that methanol can be detrimental for sour TLC pipelines even in a completely oxygen-free environment, resulting in significant localized attacks with a penetration rate much higher than the (average) mass loss rate. Therefore, it is possible that the root cause in many field cases is the methanol itself, at least if the methanol content is high. It is reasonable to believe that the combined effect of methanol and oxygen will result in an even worse condition, but efforts of removing oxygen from the methanol injection points will not remove the main problem which is methanol itself.

The mechanism of enhanced corrosion due to methanol is not yet fully understood, but it was reported that iron sulphides that formed in methanol were fragile and had poor adherence.[41,42] Therefore the protectiveness of these iron sulfides is assumed to be poor, particularly for those formed at low temperatures.[43]

The corrosion rate in a bulk phase with 50% methanol (T3 BOL) was low with little localized corrosion, while it was higher and significantly more localized for the T3 TLC coupon. High corrosion rates were reported for pure methanol with CO_2 and H_2S, and localized corrosion was promoted for 25 – 75% methanol.[41] Since methanol is more volatile than water, the condensing phase will most likely have higher methanol content than the liquid bulk phase, and this is assumed to - at least partly - explain the difference in TLC and BOL corrosion in the T3 experiment. Furthermore, the T3 BOL coupon was exposed at a much higher temperature than the TLC coupon (80°C vs. 25°C) and thus it is likely that the iron sulphide that formed was different (different morphology or different type of iron sulphide) and therefore had a more protective surface film. However, no detailed investigation of the surface film was carried out.

Although the present work is based on only a limited number of experiments and corrosion coupons, the trend is clear. Without methanol, the general sour TLC resulted in relatively uniform corrosion, but at a rate that probably is higher than most operators can accept. The present tests lasted only for 14 days and the corrosion rate may decline with time. Still, even with reduction of the corrosion rates in the long time perspective, the corrosion rates are in many cases too high for unmitigated operation. The additional presence of methanol resulted in localized corrosion with a penetration rate more than 15x the average corrosion rate, further confirming the need for enhanced corrosion mitigation of such pipelines. Such mitigation will have to be evaluated individually from pipeline to pipeline, but it can typically involve flow control to avoid stratified flow, use of continuous or batch corrosion inhibitor and enhanced corrosion monitoring on areas at risk.[1]

CONCLUSIONS

Sour top of line corrosion was simulated using a special made sample holder with internal cooling. The TLC rates were 0.2 – 0.3 mm/y for 10 bar H_2S + 10 bar CO_2. With a fixed coupon temperature of 25 °C the corrosion rate was just slightly affected by the condensation rate. The corrosion mode was uniform corrosion with no localized corrosion.

When methanol was introduced (50% by weight in the bulk liquid) the corrosion rate increased slightly to 0.4 mm/y, but significant localized corrosion occurred. The methanol-induced localized attacks were both deep (up to 220 μm attack depth after 14 days exposure) and very densely distributed.

The present demonstrated the need for careful corrosion mitigation of pipelines exposed to sour TLC, particularly if methanol is being used.

ACKNOWLEDGEMENTS

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