



CONDENSATION RATE EFFECT ON TOP OF LINE CORROSION IN CO₂ ENVIRONMENT

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ABSTRACT

This research focuses on the effect of condensation rate on top of line corrosion (TLC) for carbon steel (X65) in CO₂ environment. The experiment was conducted in a modified glass cell which simulates the TLC phenomena with tested temperature ranging from 25 °C to 55 °C and the cooling temperature was 7 °C. The corrosion rate was measured by the weight loss method and the surface morphology was examined by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray (EDX). A baseline CO₂ corrosion test was also measured simultaneously. The corrosion rate recorded for TLC was in the range from 0.76 mm/year to 1.53 mm/year. Further, the results evident that increase in condensation rate, reduces the corrosion rate which relatively lower than bottom line corrosion rate. The formation of Iron carbonate (FeCO₃), which acts as a protective layer is not fully formed and pitting was observed on the surface of the sample. In conclusion, the modified glass cell of TLC experiment was successfully done and it is found that corrosion rate increases with the water condensation rate.

Keywords: top of line corrosion, temperature, corrosion rate, carbon steel, CO₂, condensation rate.

INTRODUCTION

Top of Line (TLC) corrosion is an important phenomenon in the oil and gas production industries worldwide and it is particularly prevalent in a number of offshore and onshore operations in Asia Pacific. Regional operators that have experienced TLC corrosion failures or damage or those that are considering its effects on the design stage include Chevron Thailand, Chevron Australia (Gorgon), PTTEP, Total Indonesia, ExxonMobil Malaysia, Shell Sarawak, Tallisman Malaysia, and others [1].

TLC corrosion occurred because of heat exchange between the pipe and colder surrounding which will lead to condensation at the internal upper pipe walls. The condensed water is low in pH, but highly saturated and supersaturated with corrosion products which will increase the pH and formation of iron carbonate will occur [2]. Most of the condensed water drains to the bottom of the pipe due to gravity forces. Continuous injection of inhibitors only can be done at the bottom of the pipe, but not the top and sides which will expose them to a very corrosive environment [3]. The condensed water at the top of line become very aggressive since it combines with carbon dioxide (CO₂) and/ Acetic acid (HAc) to form acidic gases. Due to various factors, rate and mechanism of TLC cannot be predicted precisely.

Some factors that influence TLC corrosion due to CO₂ are the temperature of the gas, the temperature of the pipe wall, the total pressure of the system, the partial pressure of CO₂, the gas velocity and the condensation rate which affect the corrosion rate in a complex way [3-6].

In 1991, Gunaltun proposed that the iron concentration in the condensed water dilutes due to the continuous condensation on the existing droplet at the top of line. Failure of applied empirical models in his field cases regarding corrosion prediction made him realized that the prediction of the critical condensation rate is more important than the corrosion [7]. However, he did not

mention on how to determine the critical condensation rate. Gunaltun and Larrey concluded that the critical condensation rate lies between 0.15 ml.s/m² and 0.25 ml.s/m² [8]. Gunaltun emphasizes the importance of studying the condensation rate is essential to TLC corrosion rate. Zhang. Z and his co-workers [7] were studied few parameters that affecting the top of line corrosion such as the effect of temperature and condensation rate on the iron carbonate film. They thought that temperature is one of the important parameters as the protectiveness of the film formed depends on the temperature. While, they found that the protective film was very protective at temperatures greater than 70 °C. They believed that supersaturation occurs because the condensation rate is too low to remove the ion produced quickly [7]. Besides that, they investigate the effect of gas velocity on TLC and the result is that the corrosion rate increased as the gas velocity increased as well as the condensation rate. However, they did not propose any correlation between the parameters and the corrosion rate and their experimental result is still questionable. Since TLC is one of the most challenging corrosion problems in oil and gas industry, the established TLC mechanism was modelled by several researchers [9-13]. Singer. M. et. al [4] were successfully measured the corrosion rate of the iron sample at a gas temperature of 40 °C and found that the general corrosion rate remains constant at a fairly low value throughout the test compared to the gas temperature of 70 °C. This study is focusing on the effect of condensation rate at controlling temperature from 40 °C to 55 °C, in order to study the properties of film forming and the TLC behavior at low temperature in a modified glass cell by weight loss method. The TLC at ambient temperature also was done for a comparison purpose. Furthermore, the corrosion rate of the bottom of line corrosion also was monitored for a baseline test.



METHODOLOGY

API 5L X65 carbon steel with a chemical composition (wt.%): 0.15 C, 0.24 Si, 1.34 Mn, 0.10 Mo, 0.01 Cr, 0.01 Cu, 0.02 Ni, and Fe balance were used in this study. All samples were polished through a series of Silica carbide (SiC) paper from 60 to 600 grit. Samples are rinsed with water and followed by ethanol. Dimension of sample were recorded. For weight loss method, initial weight also were recorded.

a) Bottom of line corrosion (Baseline test)

For baseline test, a common glass cell set-up was used to monitor the corrosion rate of the sample in the test electrolyte. Linear Polarization Resistance (LPR) and weight loss method were used according to the procedure and setup based on ASTM G3 and ASTM G31. The test set-up and test matrix were used as shown in Figure-1 and Table-1 respectively. Where, WE is the working electrode (sample), RE is the reference electrode (Ag/AgCl) and AE is the auxiliary electrode.

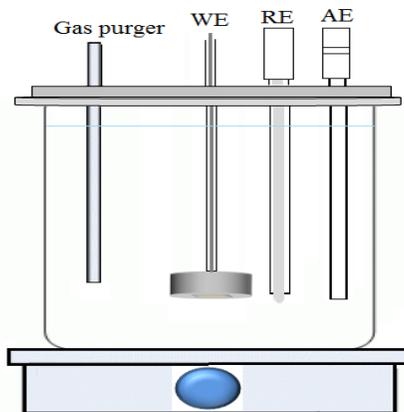


Figure-1. Glass cell set-up for baseline test.

b) TLC experiment

TLC experiments were carried out in modified glass cell. The arc shape sample was used for this test. Followings steps were involved to simulate TLC:

- Modified glass cell as illustrated in Figure-2 is set up according to test matrix shown in Table-2.
- After grinded process, the sample is placed in a holder above the NaCl solution surface.
- Cooling water is pumped into the holder from the chiller which pass through upper side of the sample.
- Temperature of NaCl solution is controlled by the hotplate to simulate the wet gas temperature in pipelines.
- The condensed water is collected through a funnel into a collector.
- Before the test, NaCl solution was deoxygenated by purging CO₂ for 1 hour and continue throughout the test. The solution is heated up to the decided temperature before starts.
- Test duration was 48 hours. After test duration, metal samples were removed, cleaned with distilled water,

dried with cold air and then weighed. The corrosion rate was measured using the weight loss data.

- SEM - EDX analyses were employed to analyze the composition and morphology of the corrosion scales.
- The collected condensed water is measured to calculate the condensation rate for each temperature.

Table-1. Test matrix for TLC test.

Parameter	Test condition
CO ₂ pressure	1 bar
Duration	48 hours
Gas flow rate	Stagnant
Electrolyte	2 liters 3 wt% NaCl
Controlling temperature	25 °C, 40 °C, 55 °C
Cooling temperature	7 °C

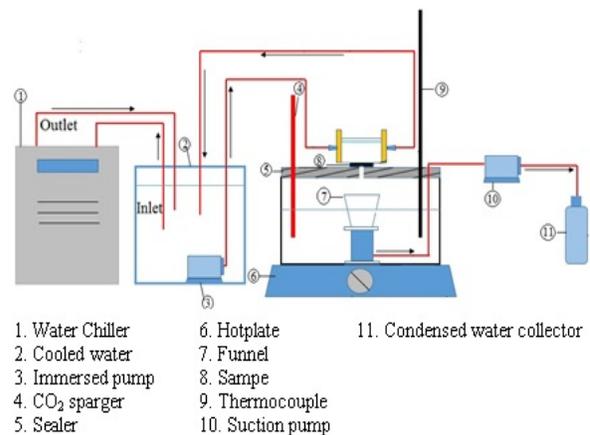


Figure-2. Schematic diagram of the TLC test.

Table-2. Test condition.

Parameter	Test condition
CO ₂ pressure	1 bar
Duration	48 hours
Gas flow rate	Stagnant
Electrolyte	2 liters 3 wt% NaCl
Controlling temperature	25 °C, 40 °C, 55 °C

RESULTS AND DISCUSSION

a) Bottom of the line corrosion (Baseline test) linear polarization resistance (LPR)

A baseline test was carried out by LPR method and the obtained corrosion rates are depicted in Figure-3. The average corrosion rate found are 1.82 mm/yr, 2.44 mm/yr and 3.30 mm/yr for 25 °C, 40 °C and 55 °C respectively. During 1st hour of testing, the corrosion rates are found to increase in all temperatures. Further, corrosion rate at 25 °C has reached almost constant value after 2 hours. In contrast, at 40 °C and 55 °C the corrosion rate increased dramatically with time and reached almost constant value only after last 30 hours of immersion. This



explained by the properties of the porous and less protective FeCO_3 layer forming at the surface of the sample at 40 °C and 55 °C. As expected, the average corrosion rate of the sample at 40 °C and 55 °C is higher than 25 °C since higher condensation rate will produce higher corrosion rate.

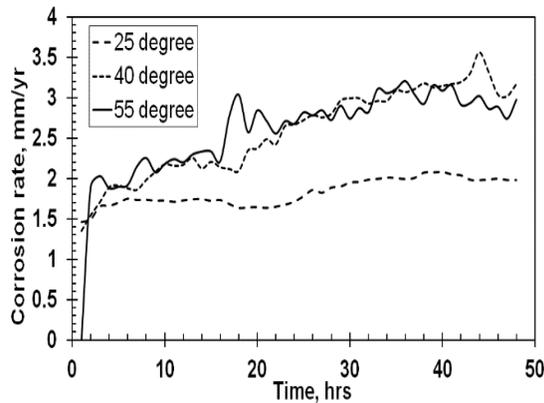


Figure-3. Baseline corrosion rate trending in CO_2 corrosion environment at tested temperature 25 °C, 40 °C and 55 °C

Weight loss measurement

Table-3 shows the weight loss result for the baseline test. The corrosion rate measured at temperature 25 °C, 40°C and 55 °C is 0.83 mm/yr, 1.96 mm/yr and 2.38 mm/yr respectively. The corrosion rate increases approximately 3 times at temperature 55°C when compared with the initial corrosion rate at 25°C of tested temperature. The increasing in corrosion rate was due to higher kinetics at the higher temperature.

Table-3. Weight loss results for baseline test.

Temp, °C	Corrosion rate, mm/yr
25	0.83
40	1.96
55	2.38

Comparison of corrosion rate by LPR and weight loss

The corrosion rate values obtained by LPR and weight loss method is shown in the bar chart (Figure-4). From the graph, it is clear that LPR method shows higher corrosion rate as compared to weight loss method. However, both method shows similar trend that increasing corrosion rate along with increasing controlling temperature.

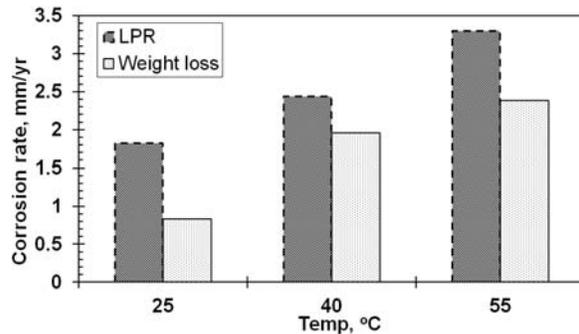


Figure-4. Bar chart of corrosion rate in CO_2 environment by weight loss method and LPR method.

b) TLC experiment

Modified glass cell test was used to simulate the TLC conditions. The temperature was set at 25 °C, 40 °C and 55 °C and the CO_2 partial pressure is at 1 bar. The initial weight of the samples were recorded. The corrosion rate measured by weight loss method and the calculated condensation rate for TLC test is listed in Table-4. The result shows that the corrosion rate of the sample with condensation rate of 0.024 g/ m^2s is 0.76 mm/yr, where the total condensation water collected is 2 ml. The pH value of the condensed water collected at the end of the experiment is 6.3 which is slightly acidic. While for condensation rate at 0.060 g/ m^2s , the corrosion rate is 1.25mm/yr. The collected condensed water is 5 ml which has pH 5.5. For condensation rate 0.097 g/ m^2s , the corrosion rate recorded is 1.53 mm/yr with 8.1 ml condensation water collected. The pH of condensation water is 5.7. Figure-5 shows that as the condensation rate increase, the corrosion rate also increased which implies that the presence of condensed water layer on pipe wall is the factor that contributes to corrosion process. In the absence of condensed water layer, the top of line corrosion cannot occur. Literature [2,14-15] evidenced that, when the condensation rate is low, the corrosion products accumulate rapidly in condensed water until the water is saturated which will lower the pH. When the condensed water is supersaturated with FeCO_3 , a protective film will form on the surface which lowers the corrosion rate. At high condensation rate, saturation cannot be reached because high condensation rate implies more water available, more ions can be dissolved, therefore corrosion rate value increase.

Table-4. Weight loss result for TLC environment.

Temp (°C)	Weight loss (g)	Corrosion rate (mm/year)	Condensation rate (g/ m^2s)	pH
25	0.0454	0.76	0.024	6.3
40	0.0825	1.25	0.060	5.5
55	0.0920	1.53	0.097	5.7

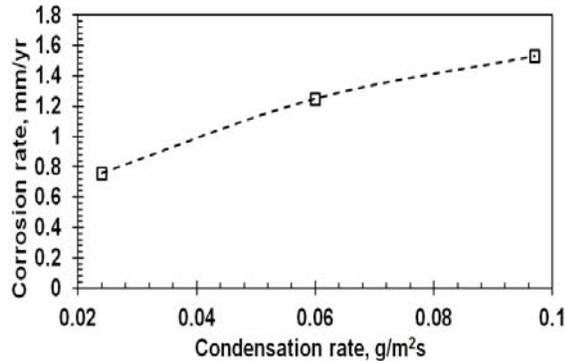


Figure-5. Plotted graph of corrosion rate at a different condensation rate.

Scanning electron microscope (SEM) analysis

The surface morphology of the samples for TLC were analysed by SEM right after the end of the test. In addition, the EDS investigations was carried out in order to identify the elemental composition of the species tabulated on the sample surface after exposure to the test environment. The crosshair in the SEM images indicates the position which EDS analysis was taken.

At 25 °C

At low condensation rate ($T_s = 25^\circ\text{C}$), the samples had some grey film formed on the surface. This observation is typical for TLC experiments, which is probably due to the pattern of the corrosion process under dropwise condensation. Some spot of underlying sample found covered by the FeCO_3 layer, while some pitting were also observed and even there are some spots is not corroded as marked in Figure-6. Table-5 shows the percentage of each element tabulated on the sample surface.

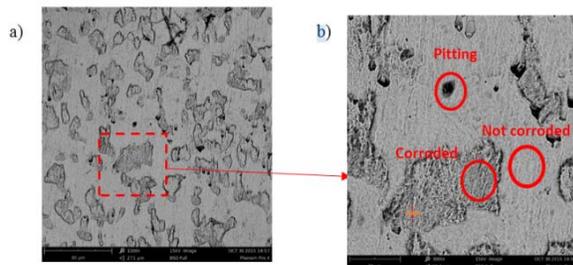


Figure-6. SEM image for X65 steel under $T = 25^\circ\text{C}$ environment at magnification: a) 1000X, b) 3000X.

Table-5. EDS results at $T = 25^\circ\text{C}$.

Element Number	Element	Weight %
6	C	4.0
8	O	4.2
26	Fe	91.8
	Totals	100.00

At 40 °C

Figure-7 shows the SEM image of metal samples after the immersion test. Localized corrosion was the main failure found over the metal surface. The grain boundaries were clearly observed on the sample surface. EDS result in Table-6 confirmed the existence of a dense iron carbon film.

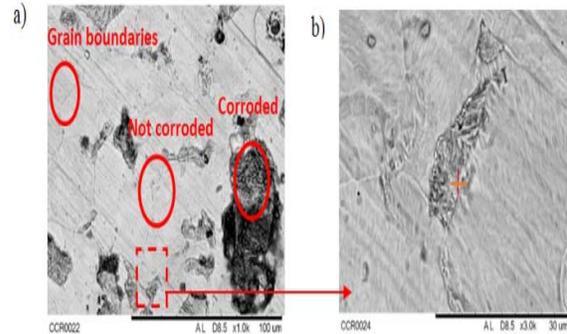


Figure-7. SEM image for X65 steel under $T = 40^\circ\text{C}$ environment at magnification: a) 1000X, b) 3000X.

Table-6. EDS results at $T = 40^\circ\text{C}$.

Element Number	Element	Weight %
6	C	8.21
8	O	12.75
26	Fe	73.99
25	Mn	2.66
14	Si	2.4
	Totals	100.00

At 55 °C

At temperature 55°C , not fully formed crystals (corrosion products) were observed on the metal surface, which are identified by EDS (Table-7) to be FeCO_3 . In this high condensation rate, FeCO_3 become increase in magnitude and denser compared to the other two tested temperature (25°C and 40°C) at center of the sample. Localized corrosion is pronounced throughout the test. A number of pits were observed on the sample surface.

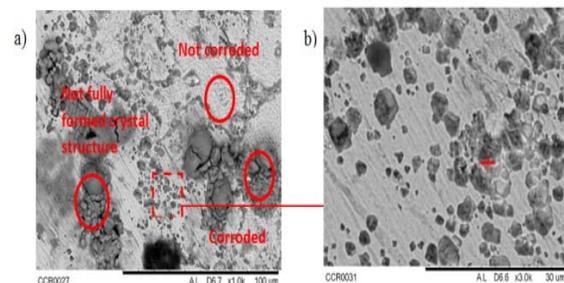


Figure-8. SEM image for X65 steel under $T = 55^\circ\text{C}$ environment at magnification: a) 1000X b) 3000X.

**Table-7.** EDS results at T = 55 °C.

Element Number	Element	Weight %
6	C	6.29
8	O	8.68
26	Fe	83.01
11	Na	1.43
14	Si	0.60
	Totals	100.00

c) Overall corrosion rate

Table-8 shows the overall corrosion rate of sample in TLC and bottom of line corrosion. For metal in bottom of line, it is found that when temperature increases from 25 °C to 55 °C, the corrosion rate increases from 1.82mm/year to 3.27 mm/year. Weight loss method shows the same pattern in corrosion rate. At 25 °C, the corrosion rate recorded is 0.83 mm/year and it increases up to 2.38 mm/year at 55°C. TLC shows lower corrosion rate as compared to CO₂ corrosion environment. This is due to the formation of FeCO₃ from the supersaturated condensing water and the corrosion product which act as a protective layer to reduce corrosion rate at TLC environment.

d) Discussion

Weight loss experiment shows that as the condensation rate increase, the corrosion rate increase which obeys the theory of corrosion rate due to condensation rate. At low condensation rate, saturation of condensation water with the corrosion product can occur which lowers the pH and layer of iron carbonate may exist. At high condensation rate, saturation cannot be reached and corrosion rate can reach to several mm/year.

Table-8. Corrosion rate for baseline and TLC condition.

Temperature (°C)	Corrosion Rate (mm/year)		
	(Baseline)		TLC
	LPR	WL	WL
25	1.82	0.83	0.76
40	2.55	1.96	1.25
55	3.27	2.38	1.53

In condensation condition, corrosion product can continuously accumulate on the sample due to the high level of supersaturation, which leads to the modification of the surface morphology. The acidic environment promotes the Fe dissolution and increase the pH, so that nearly crystal film was observed on the sample at higher temperature.

The presence of the corrosion product was controlled by the temperature throughout the test. The nature of the condensation process in the top of the line under the tested condition explains the non-uniform distribution of iron carbonate. It can be confirmed by the increase of corrosion rate while increase test temperature.

Increase the temperature from 25 °C to 40 °C enhance corrosion rate upto 39.2 %. While, rise of temperature from 40 °C to 55 °C increases corrosion rate to 18.3 %.

CONCLUSIONS

The study of TLC at various condensation rates were successfully done. Results shown that increasing in temperature will increase the condensation rate which subsequently enhances the corrosion rate. The corrosion rate is higher at 55 °C than at 40 °C and this behavior is observed both at conditions (TLC and bottom of the line). Further, SEM analysis shows that there is not fully formed FeCO₃ layer on the surface in both exposure conditions. Pitting formation on the steel surface was also found which evidenced the corrosion is localized and can be dangerous to pipeline in long term.

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