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Ethane Feeder Pipeline Corrosion Rate Prediction Analysis

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Abstract: Carbon dioxide CO_2 is one of the major gases of concern in ethane feeder pipeline since it presence will induce corrosion which then damage the pipeline. The purpose of this study is to determine the corrosion rate using NORSOK M-506 commercial software prior to comparing corrosion rate with international standard, identify optimum level to control corrosion rate, and analyse the relationship of moisture content towards H_2CO_3 impact and its pH level for variety of CO_2 concentration, temperature, pH and moisture content in the ethane feeder pipeline. Evaluation impact was done for CO_2, temperature and pH value using average value and is categorised as moderate between 0.025 to 0.12 mm/year as per an International Standard – National Association of Corrosion Engineer (NACE). Corrosion rate for CO_2 is 0.055 mm/year while for temperature and pH are 0.054 mm/year and 0.055 mm/year respectively. Based on the average corrosion rate of 0.05 mm/year, the simulation results produce the optimum corrosion control level when CO_2 concentration is 1.40 mole percent at temperature of 21.5 °C and pH of 4.7. Since NORSOK M-506 software has the limitation of pH coverage within 3.5 – 6.5, moisture effect is analysed using chemistry equation approach. It was found that the concentration of H_2CO_3 increases with moisture content. More H_2CO_3 formation in pipeline will definitely promote a more serious internal corrosion.

Keywords: Chemical reaction; Corrosion control; Corrosion rate; Corrosivity; Feeder pipeline.

1. INTRODUCTION

Corrosion causes metal wear due to the chemical reaction between a metal body and environments, particularly in a dynamic situation such as pipeline [1]. Carbon dioxide (CO_2) gas is one of the significant contributing factors that causes corrosion and degradation of pipelines in the oil and gas industry [2-6]. Huge costs are directed annually to alleviate and manage corrosion [7-9]. Predictive tools for material loss prediction or material selection can be derived from empirical and mechanistic equations based on environmental condition. In an ethylene processing line, the presence of other factors such as moisture, temperature, and pH level are known to induce corrosion but the actual mechanism in CO_2 environment is still not fully understood while corrosion is generally poorly understood. CO_2 can dissolve in water to form carbonic acid (H_2CO_3) and will lower the pH. Sufficient quantities of H_2CO_3 can promote general corrosion and/or pitting corrosion of carbon steel [2, 10-11]. In order to evaluate these interactions, corrosion rate prediction in ethane feed pipeline should be studied.

Carbon dioxide related corrosion is one of the major challenges in oil and gas industry since produced formation fluids contain corrosive gases including CO_2 [8, 12-13]. Moreover, applications of various modern production enhancement technologies such as Enhanced Oil Recovery (EOR) require injection of CO_2 gas into reservoirs. The presence of CO_2 with other gas impurities such as hydrogen sulphide (H_2S), carbon monoxide (CO), sulphur dioxide (SO_2), and oxygen (O_2) in production stream can result in corrosion of well casing and production tubing [14]. Dry CO_2 gas is considered less corrosive than wet CO_2, which reacts with free or condensate water to form carbonic acid [10, 15]. Consequently, damage can occur in the form of uniform or localised corrosion [14]. CO_2 corrosion is a complex process, which is affected by CO_2 partial pressure, temperature, water chemistry, and pH [1, 16-18]. A number of theoretical and experimental studies has been conducted to have better understanding on CO_2 corrosion [19-21]. Various CO_2 corrosion models have been developed and used in the industry to mitigate the said corrosion problem. However, most of these models are suitable for low-pressure applications [22].

This study is aimed to determine corrosion rate using NORSOK M-506 [23] commercial software prior to comparing corrosion rate with international standard, identify optimum level to control corrosion rate, and analyse the relationship of moisture content towards H_2CO_3 impact and its pH level for variety of CO_2 concentration, temperature, pH and moisture content in the ethane feeder pipeline.

2. METHODOLOGY

The first part basically discussed the simulation which was undertaken in order to simulate corrosion rate using NORSOK software for each of three factors which were CO_2 concentration, pH and temperature based on their true data. This followed by analysis where the findings were being described in a numerical value. The second part was to calculate H_2CO_3 concentration based on moisture content level in ethane feeder pipeline using chemistry equation approach.

2.1 CO_2 Corrosion Rate Calculation Modelling

The model is an empirical corrosion rate model for carbon steel in water containing CO_2 at different temperatures, pH, CO_2 fugacities, and wall shear stresses as shown in general Equation (1). It is based on flow-loop experiments at temperatures of 5 °C as in Equation (2), 15 °C in Equation (3) until 160 °C. A large amount of data at various temperatures, CO_2 fugacities, pH, and wall shear stresses were used.

The main bulk of the flow-loop tests used in developing the calculation model was taken from the research programs by Institute for Energy Technology (IFE) in Norway. The main principles for the testing were described by [18].

$$CR = K_t \times f_{CO_2}^{0.62} \times \left(\frac{S}{19}\right)^{0.146+0.324 \log f_{CO_2}} \times f(PH)_t \tag{1}$$

The following equation is used at temperature 5 °C:

$$CR_t = K_t \times f_{CO_2}^{0.36} \times f(PH)_t \tag{2}$$

The following equation is used at temperature 15 °C:

$$CR_t = K_t \times f_{co_2}^{0.36}\, x \left(\frac{s}{19}\right)^{0.146+0.324 \log f_{CO_2}} \times f(PH)_t \tag{3}$$

where CR_t is the corrosion rate at temperature t in mm/year, K_t is the constant for the temperature t used in corrosion rate calculations, f_{CO2} is the fugacity of CO_2 in bar, S is the wall shear stress in Pa, and $f(PH)_t$ is a pH factor at temperature t. The corrosion rate between temperatures where constant K_t has been generated [23] is found by a linear extrapolation between the calculated corrosion rate at the temperature above and below the desired temperature. In this study, the input parameters used to calculate the corrosion rate was obtained from true data (measured at site) which consists of CO_2 concentration and temperature. Meanwhile for the pH value, it was calculated using NORSOK simulation which then verified with true data. On top of that, several assumptions were also established for the other parameters such as shear stress at 1 bar, glycol concentration of 0%, and inhibitor efficiency of 95%. In order to simulate the corrosion rate due to CO_2 effect, variable parameters such as pH and temperature were calculated based on their average value and taken as constant. A similar approach was also applied for the temperature and pH effects. The details of the procedures applied to determine the input parameters are as follows:

a) Ethane Feeder Pipeline Content Determination

CO_2 concentration is determined by Gas Chromatograph (GC) as shown in Figure 1. A sample is injected into the GC and travels down a flowing carrier gas (usually nitrogen or helium). The light components travel down the tube more quickly and are the first detected. Over the next few minutes, all of the components exit the column and are measured by the detector. A diagram of the key components of a gas chromatograph generated is shown in Figure 2. The area under each of the peaks is proportional to the concentration of the compound presents in the sample. Like most analytical techniques, calibration gas sample must be measured so that the process gas concentrations can be properly calculated.

This test method covers the determination of carbon dioxide, methane, ethane, acetylene, and other hydrocarbons in high-purity ethylene. Hydrogen, nitrogen, oxygen, and carbon monoxide are determined in accordance with ASTM D2504-88 [24]. The percent of ethylene is obtained by subtracting the sum of the percentages of the hydrocarbon and non-hydrocarbon impurities from 100. The method is applicable over the range of impurities from 1 to 500 parts per million volume (ppmV).

The sample is separated in a gas chromatograph system utilising four different packed chromatographic columns with helium as the carrier gas [25]. Methane and ethane are determined using a silica gel, while propylene and heavier hydrocarbons are determined using a hexamethyl phosphoramide (HMPA) column. Acetylene is determined using, in series, a hexadecane column and asqualane column. Carbon dioxide is determined using a column packed with activated charcoal impregnated with a solution of silver nitrate in β,β`oxydipropionitrile.

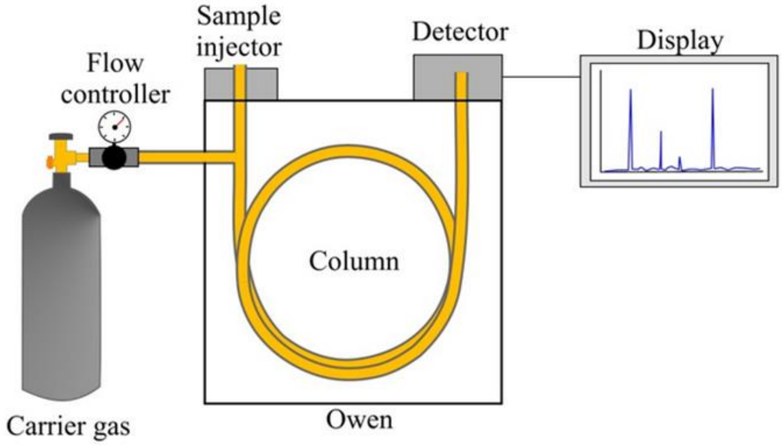

Figure 1. Schematic diagram of gas chromatography

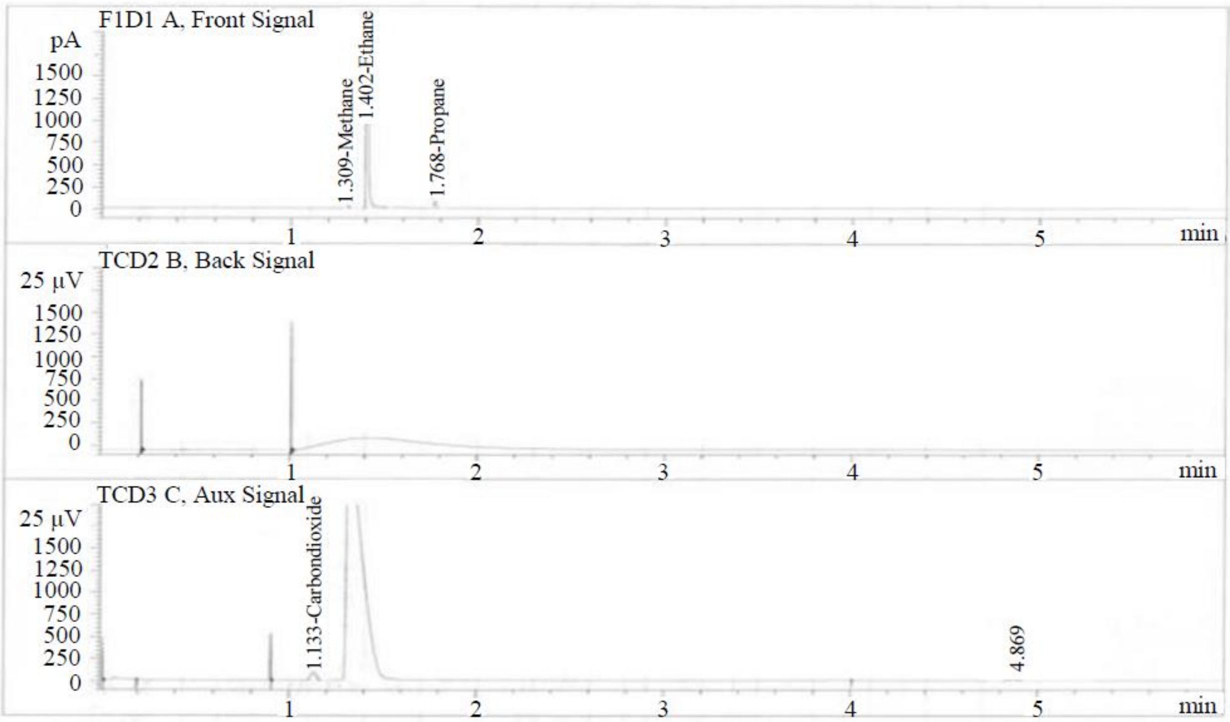

Figure 2. Chromatogram for CO_2 by gas chromatography

Columns other than those mentioned above may be satisfactory. Calibration data are obtained using standard samples containing the impurities, carbon dioxide, methane, and ethane in the range expected to be encountered. Calibration data for acetylene is obtained by assuming that acetylene has the same peak area response on a weight basis as methane. The acetylene content in a sample is calculated on the basis of the ratio of peak area of the acetylene peak to the peak area of a known amount of methane. Calculations for carbon dioxide, methane, and ethane are carried out by the peak-height measurement method.

b) Ethane Feeder Pipeline Temperature Measurement

The temperature is measured by a thermocouple at site and recorded in a distributed control system. A thermocouple comprises at least two metals joined together to form two junctions [26]. One is connected to the body whose temperature is to be measured; this is the hot or measuring junction. The other junction is connected to a body of known temperature; this is the cold or reference junction. Therefore, the thermocouple measures unknown temperature of the body with reference to the known temperature of the other body.

c) Determination of pH

The calculated pH was obtained from simulation while verification of pH could be done experimentally by passing through ethane gas in a gas scrubber as shown in Figure 3. New pH papers were placed on scrubber internal wall and let the sample gas passing through for 10 minutes.

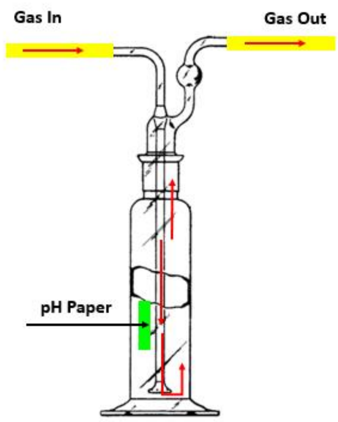

Figure 3. Schematic diagram of pH paper in a glass scrubber

If there was any change in colour experienced by the pH paper, it should be recorded and compared with the standard Colour pH Strip. Safety precaution should be taken especially safety glass is mandatory to be worn. Gas flow should be regulated accordingly.

The pH paper is used to determine if a solution is acidic, basic, or neutral. This is determined by dipping part of the paper into a solution of interest and watching the color change. If the paper turns a dark greenish-blue, the pH may likely be around 11 to 14. The term stands for potential hydrogen and is a measurement of how many hydrogen ions, symbolized as H^+, are in a solution. The more hydrogen ions present in a substance, the more acidic it is. A high number of hydroxide ions, symbolized as OH^-, characterize basic or alkaline substances. If a substance has the same amount of H^+ and OH^-, then it is said to be neutral. Water is a common example of this sort of solution. In this study, even though the sample itself is in a gas form, however, the moisture content in the said gas sample may good enough to give an opportunity for pH detection.

2.2 H_2CO_3 Concentration Determination

Moisture in gas sample is measured by a shaw meter. The sample is introduced to the shaw meter direct from the sampling point outlet at site. The water or moisture content is conducted by in-situ measurement using shaw automatic dew point meter (SADP) as shown in Figure 4.

According to Acid-based Chemistry, Bronsted/Lowry Acid theory [27], an acid is a substance which can donate a hydrogen ion (H^+) or a proton while a base is a substance that accepts a proton. Acids are usually referred to as donating protons, or H^+, while bases donate OH^-, or hydroxyls. The proton is strongly bound to water forming the basic unit of H_3O^+, the hydronium ion. The usage of H_3O^+ is usually reserved to reactions involving water. The reaction for water is shown in Equation (4). The dissociation (equilibrium) constant, K_a is referred to the reaction when an acid donates a proton to water and its formula is shown in Equation (5).

$$H_2O <=> H^+ + OH^- \tag{4}$$

$$K_a = [H^+]\,[OH^-]/[H_2O] \tag{5}$$

H_2CO_3 dissociates in a stepwise manner, furnishing one proton at a time. For this reason, pH is determined using $[H_3O^+]$ for the first dissociation as Equation (6). For H_2CO_3, K_a is normally referred to 4.3×10^{-7} which is under first dissociation as shown in Equation (7). Concentration of H_2CO_3 should be calculated before determining the pH value. When CO_2 gas is in contact with H_2O, the chemical reaction as illustrated in Figure 5 will take place to produce H_2CO_3.

Figure 4. A shaw automatic dew point meter

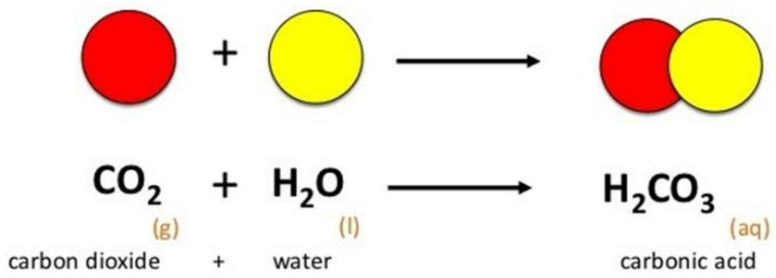

Figure 5. Chemical reaction of carbonic acid formation

$$H_2CO_3 + H_2O <=> H_3O^+ + HCO^{3-} \quad (6)$$

$$K_a = [H_3O^+]\,[HCO^{3-}]/[H_2CO_3] \quad (7)$$

The chemical equation of two reactants combine to produce a single product is balanced. One mole of CO_2 will react with one mole of moisture to produce one mole of H_2CO_3 [28-29]. However, by considering concentration unit of moisture with part per million (ppm) volumes is much lower than CO_2 in percent [30], a complete chemical reaction tended CO_2 becomes excess. In this chemical reaction, reactants (CO_2) which are not used up when the reaction has completed is shown as excess reagents. The reagent (H_2O) which has been completely used up or reacted is shown as the limiting reagent, because its quantity limits the amount of products formed. Since H_2O is a limiting reagent, the concentration of H_2CO_3 is mainly affected by moisture content. Generally, corrosion rate increases with moisture content because more H_2CO_3 is generated through electrochemical reaction in the pipeline system.

3. RESULTS AND DISCUSSION

3.1 CO_2 Corossion Rate Calculation Modelling

a) The Effect of CO_2 Concentration on Corrosion Rate

A total of 50 CO_2 concentration data were collected for a duration of 50 days and the trend was tabulated as shown in Figure 6. Based on the trending itself, the highest concentration recorded was 2.13 mole % and the lowest was 1.24 mole %. The fluctuation of CO_2 concentration level could promote corrosion activity if the control mechanism was not supported. In order to understand the effect of CO_2 level towards corrosion impact, corrosion rate can be simulated using commercial software NORSOK M-506, a recommended practice for calculation of corrosion rate in hydrocarbon production and process systems where the corrosive agent is CO_2. The corrosion rate trending for various CO_2 concentrations is illustrated in Figure 7. Figures 6-8 show that corrosion rate is directly proportional to CO_2 concentration and CO_2 partial pressure (PCO_2).

As seen in Figure 8, an increase of CO_2 partial pressure could promote an increase in corrosion rate. This is due to the increase in H_2CO_3 concentration which accelerates the cathodic reaction, and ultimately the corrosion rate [31]. However, when other conditions are favourable for formation of iron carbonate scales, an increase in PCO_2 concentration can produce a favourable effect. At a high pH, higher PCO_2 would increase bicarbonate and carbonate ion concentrations and subsequently produces a higher super saturation, which accelerates precipitation process and scale formation. If there was no corrosion film formed on the metal surface during the corrosion process, increasing further the partial pressure of CO_2 will cause an increase in corrosion rate.

According to National Association of Corrosion Engineers (NACE) [32], a worldwide corrosion authority, the qualitative categorisation of carbon steel corrosion rate for oil production system is as shown in Table 1. Referring to corrosion rate prediction on CO_2 concentration, it is concluded that CO_2 level at ethane feeder line was quantitatively categorised under moderate condition where the corrosion rate was between 0.025–0.12 mm/year as shown in Figure 9. By average, the corrosion rate was 0.055 mm/year which could be considered as moderate.

The corrosion rate for CO_2 was categorised as moderate and should be controlled so that it will fall between 0.025–0.12 mm/year with suggested value of 0.05 mm/year. Based on NORSOK simulation study, the level of CO_2 concentration that giving corrosion rate of 0.05 mm/year is 1.40 mole % as shown in Figure 10. The optimum CO_2 concentration of 1.40% could be a setting to control the corrosion rate which shall not exceed 0.05 mm/year. Even though it is still within the moderate zone but by referring to the moderate range of 0.025–0.12 mm/year, 0.05 mm/year is representing mid-point from this control range.

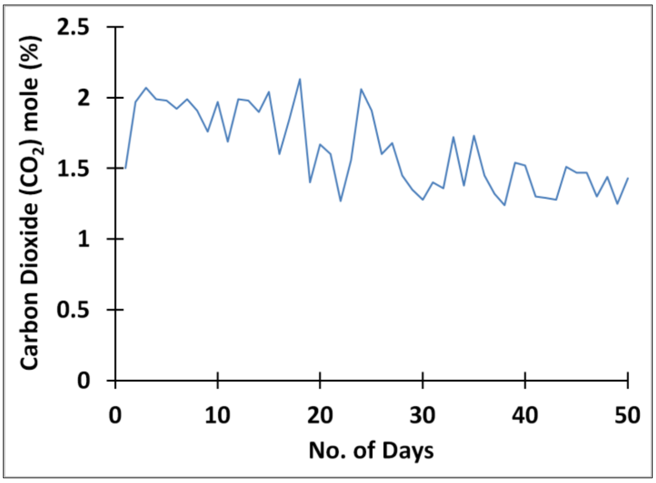

Figure 6. CO_2 concentration trend

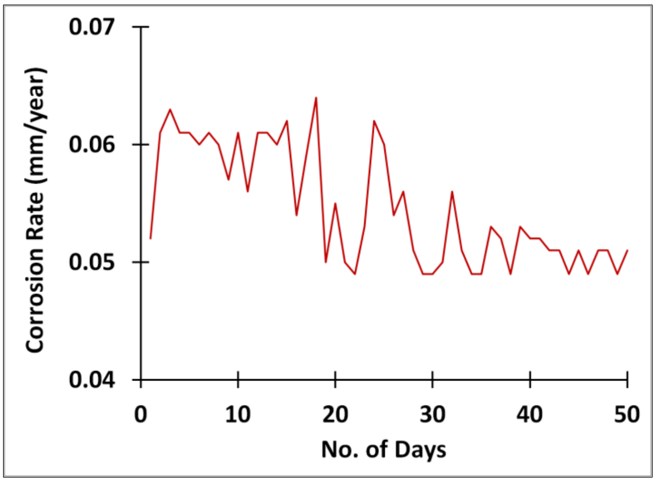

Figure 7. Corrosion rate trend

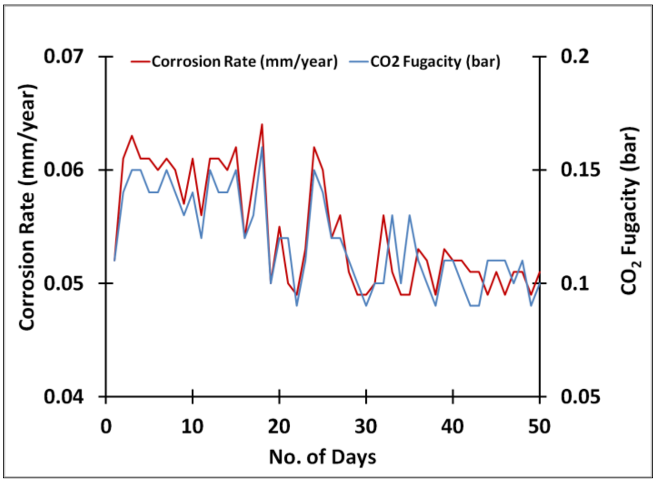

Figure 8. CO_2 partial pressure and corrosion rate trend

Table 1. Qualitative categorisation of carbon steel corrosion rates for oil production system [32]

Category	Average corrosion rate, mm/year
Low	< 0.025
Moderate	0.025 – 0.12
High	0.13 – 0.25
Severe	> 0.25

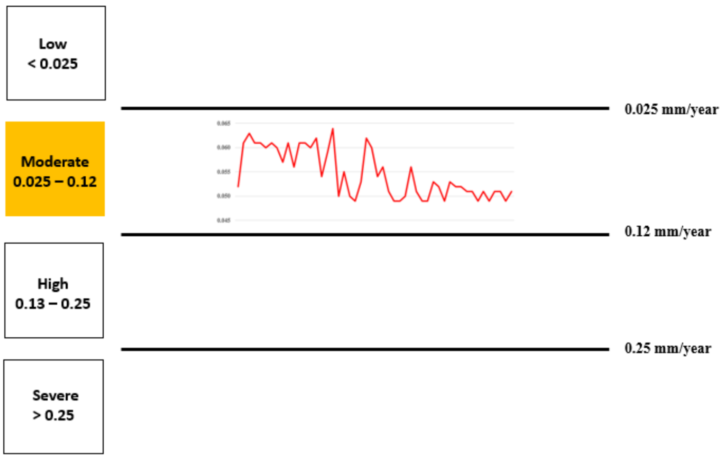

Figure 9. CO_2 corrosion rate as compared with NACE standard

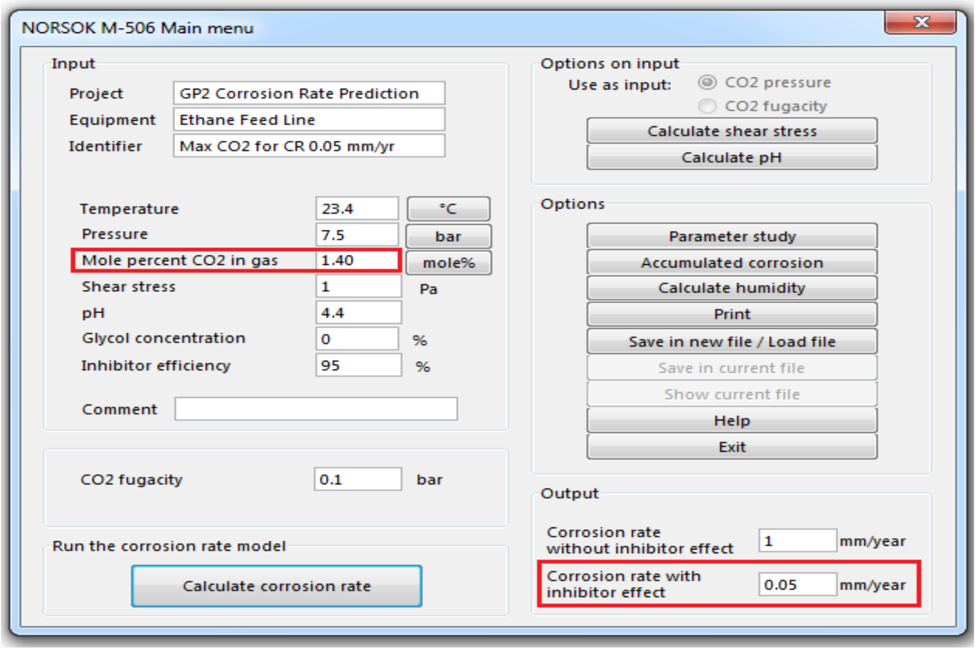

Figure 10. NORSOK M-506 simulations for max CO_2–corrosion rate of 0.05 mm/yr

b) The Effect of Temperature on Corrosion Rate

Based on simulation, the lowest temperature is 21.1 °C and the highest is 25.4 °C from 50 recorded data and trending as illustrated in Figure 11. The trending shows that the fluctuation of temperature is relatively stable within 21.0 °C – 26.0 °C and most of the temperature recorded at higher side which is above 23 °C.

Corrosion rate due to temperature effect at ethane feeder pipeline was simulated as illustrated in Figure 12. The highest temperature of 25.4 °C and the lowest temperature of 21.1 °C had been recorded during the data collection period and both temperatures were promoting corrosion rate between 0.051 – 0.059 mm/year. Conclusively, the corrosion rate is found to be directly proportional with temperature.

Based on the international standard of temperature effect on corrosion rate, it can be seen that temperature effect on ethane feeder line is quantitatively categorised under moderate condition where corrosion rate is between 0.025–0.12 mm/year or an average of 0.054 mm/year as shown in Figure 13. Based on NORSOK simulation study, corrosion rate of 0.05 mm/year can be controlled with temperature at 21.5 °C.

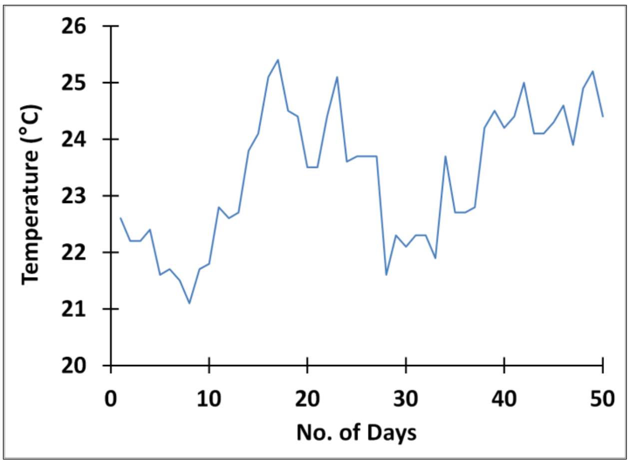

Figure 11. Temperature at ethane feeder pipeline

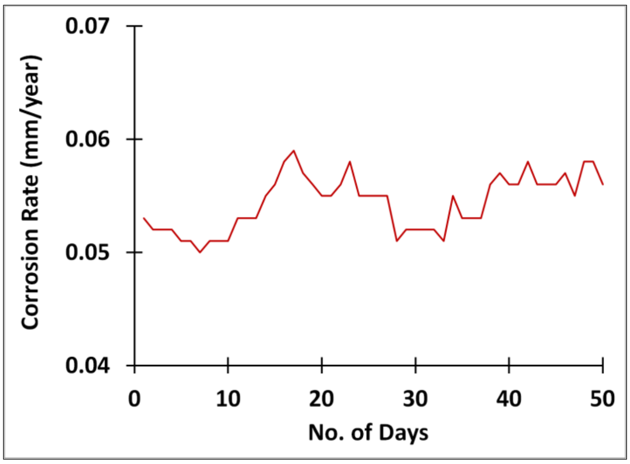

Figure 12. Corrosion rate at ethane feeder line

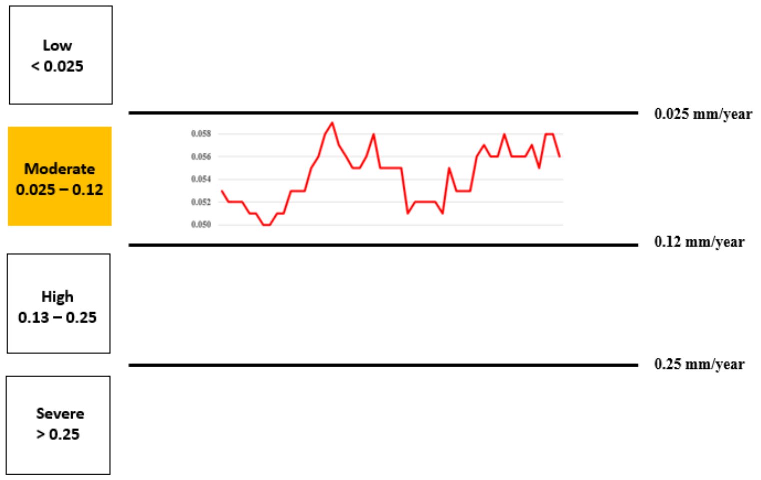

Figure 13. Comparison corrosion rate due to temperature effect with NACE standard

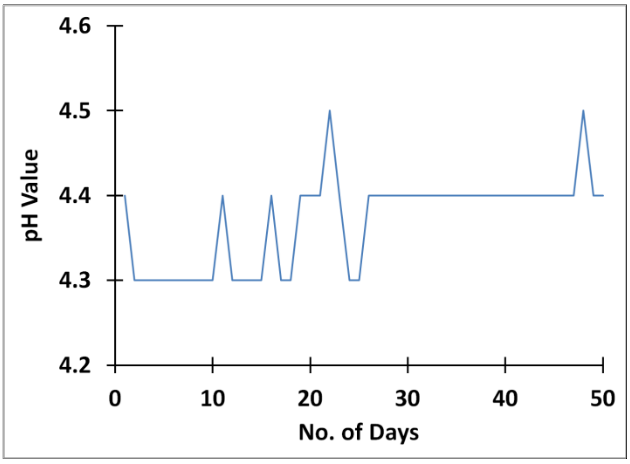

Figure 14. pH reading at ethane feeder line

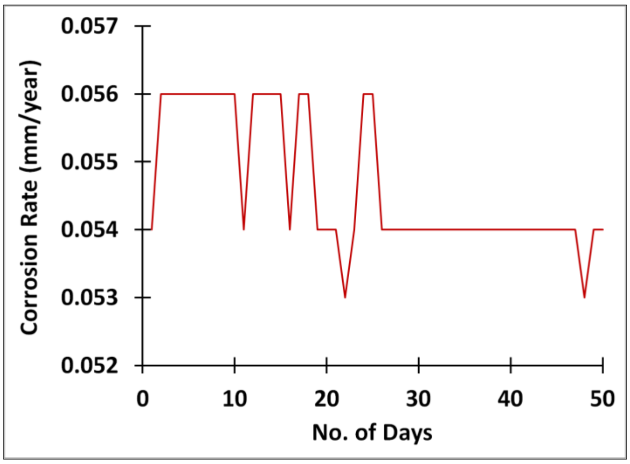

Figure 15. Corrosion rate at ethane feeder line

c) The Effect of pH on Corrosion Rate

The effect of pH on corrosion rate as given by NORSOK model is dependent on temperature. Based on simulated study at shear stress of 1 bar; 0% glycol concentration, and inhibitor efficiency of 95%, pH reading of the ethane feeder line is illustrated in Figure 14 while Figure 15 shows a contrasting profile between the corrosion rate increases while pH decreases over the duration of study (i.e., corrosion rate increases as pH decreases). Lower pH is an indicator of higher acidity of the fluid.

Figure 16 shows that the average corrosion rate due to pH is in the range of 0.025–0.12 mm/year with an average of 0.055 mm/year. Therefore, quantitatively corrosion rate at ethane feeder line due to pH can be categorised as moderate and should be controlled within 0.05 mm/year. And based on NORSOK simulation study, that rate can be achieved at pH of 4.7.

3.2 H_2CO_3 Concentration

a) The Effect of Moisture Content on Corrosion Rate

Testing was conducted at site using the shaw meter and the apparatus arrangement is as illustrated in Figure 17. The measured moisture content and calculated concentration of H_2CO_3 and pH (due to moisture content) at the ethane feeder line are shown in Table 2. Based on data in Table 2, H_2CO_3 concentration at ethane feeder line are found to be directly proportional to moisture content. In addition, increased in H_2CO_3 concentration will lower the pH value.

One of the most influential parameters which affects CO_2 corrosion is water chemistry. When CO_2 dissolved in water, it is partly hydrated and forms carbonic acid. The speciation can vary from very simple, with only a few carbonic species present, as in the case with condensed water in gas pipelines. The research findings show that the water content has significant impact on concentration of H_2CO_3 as shown in Table 2. When the moisture content is high, the concentration of H_2CO_3 increases. Increase in H_2CO_3 formation in pipeline will definitely promotes more internal corrosion.

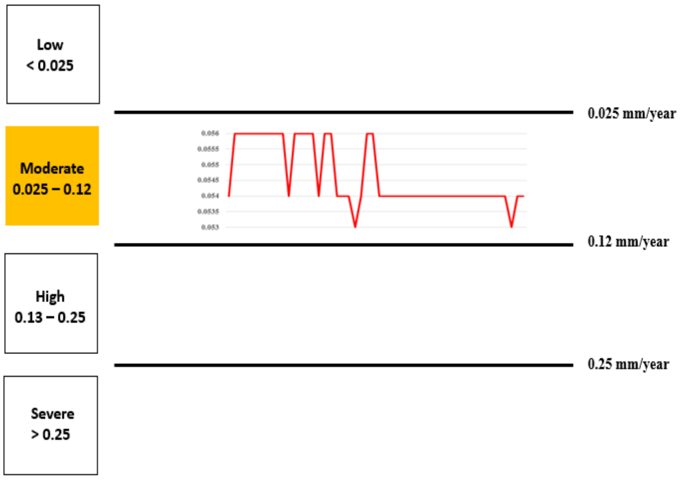

Figure 16. Categorisation of corrosion rate due to pH at ethane feeder line

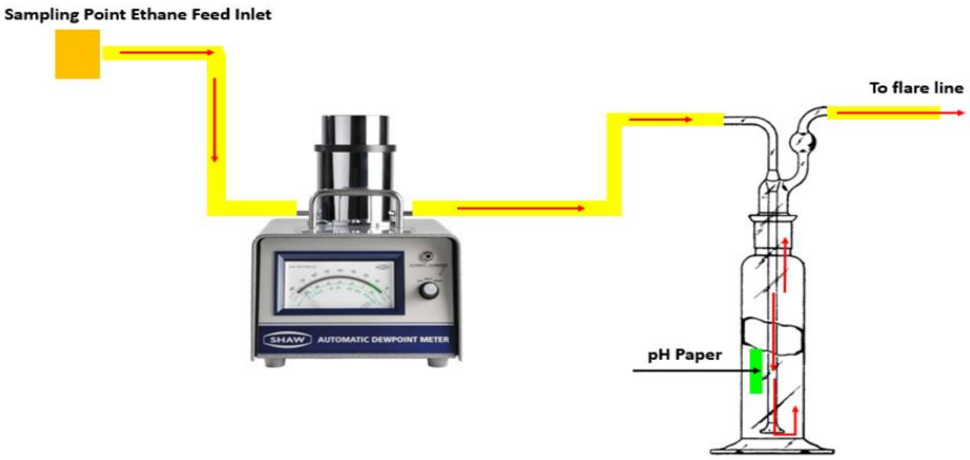

Figure 17. Apparatus arrangement for moisture and pH measurement at site

Table 2. Moisture effects towards H_2CO_3 concentration and pH level

No. of Days	ppm of H_2O	mg of H_2CO_3	pH
1	4.4	15.4	2.86
2	3.4	11.9	2.92
3	8	28.0	2.73
4	8	28.0	2.73
5	10	35.0	2.68
6	8.5	29.8	2.72
7	3.4	11.9	2.92
8	8.5	29.8	2.72
9	10	35.0	2.68
10	9.2	32.2	2.70

4. CONCLUSION

Corrosion rate at ethane feeder line is directly propositional to the CO_2 content and temperature. The higher the CO_2 concentration, the higher corrosion rate will be. CO_2 is a corrosive reactant and it will generate carbonic acid when combined with water. Higher temperature accelerates all the processes involve in corrosion and as a result, corrosion rate will increase. However, corrosion rate produces a contrasting profile as compared to pH. Generally lower pH level promotes higher corrosion rate. This phenomenon is valid because lower pH level generates more H^+ and promotes more chemical reactions.

According to NACE, corrosion rate prediction based on CO_2 concentration, temperature, and pH level can be quantitatively categorised under moderate condition if corrosion rate is between 0.025–0.12 mm/year. By average, the corrosion rate due to CO_2 effect is 0.055 mm/year, temperature effect is 0.054 mm/year, and pH level effect is 0.055 mm/year.

Based on the average corrosion rate, it is around 0.05 mm/year and these research findings provide an opportunity to identify the optimum control level (mole % of CO_2: 1.40; temperature: 21.5 °C, pH: 4.7) for these three contributing factors.

Based on simulation work using NORSOK M-506 software and acid-base theory to calculate H_2CO_3 concentration when CO_2 dissolves in water (condensed), it is partly hydrated and forms carbonic acid. The results show that the water content has significant impact on the concentration of H_2CO_3. When the moisture content is high, the concentration of H_2CO_3 increases. Generally, an increase in the formation of H_2CO_3 in pipelines will definitely promote a more severe internal corrosion.

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