

Screening and Benchmarking of Commercial Corrosion Inhibitors for Organic Acids Corrosion Mitigations

Almila Hassan¹, Khairulazhar Jumbri^{1,*}, Mohd Sofi Numin¹, Kok Eng Kee², Noorazlenawati Borhan³, Nik Mohd Radi Nik Mohamed Daud³, Azmi Mohammed Nor³, Muhammad Firdaus Suhor³

¹ Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

- ² Department of Mechanical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
- ³ PETRONAS Research Sdn Bhd, 43000 Bandar Baru Bangi, Selangor, Malaysia

ARTICLE INFO	ABSTRACT
Article history: Received 18 November 2022 Received in revised form 18 January 2023 Accepted 25 January 2023 Available online 4 February 2023 Keywords: Corrosion inhibitors; metal steel; carbon	More aggressive reservoir conditions, such as higher concentrations of CO ₂ corrosive gases, have a massive effect on corrosion. Moreover, additional aqueous species, such as organic acids, have complicated the conditions and enhanced corrosion to the maximum rate. This study investigates and screens three commercial corrosion inhibitors on their performance in mitigating corrosion at welded areas of carbon steel in high CO ₂ conditions with the presence of organic acids. These investigations were conducted via chemical elucidations to study the functional groups present in the compounds that affect the inhibition performance and the electrochemical measurements to evaluate the inhibition activities and efficiency of these commercial inhibitors under extreme conditions of high CO ₂ and organic acids. The results indicated that only CT5727 and CT17906 gave a high inhibition efficiency of 90% in the absence and presence of organic acid, while CT17906 gave the lowest corrosion rate of 0.038 mmpy in the absence of organic acid, while CT17906 gave the lowest corrosion rate of 1.00 mmpy in organic acid condition. On the other hand, D4305 gave the worst inhibition performance under both conditions. The elucidation of these inhibitors also found that specific functional groups such as hydroxy, carboxylic acid, alkyl and alkene presence in the structure were believed to affect the inhibition performance of these
dioxide; organic acid; inhibition efficiency	commercial inhibitors in mitigating corrosion. These could be used as a future reference for the new development of corrosion inhibitors in similar conditions.

1. Introduction

Corrosion is encountered in all production and transportation facilities and has become a potential natural hazard to the industry [1]. The presence of contaminants causes severe corrosion in the inner wall of pipelines. Continuous effects of corrosion can reduce the thickness of the walls, reduce the strength of pipelines, and lead to leakage accidents [2]. Carbon mild steels are the most commonly used material in building pipelines due to their ability to be assembled underwater to

* Corresponding author.

https://doi.org/10.37934/aram.102.1.1031

E-mail address: khairulazhar.jumbri@utp.edu.my

carry oil and gas hydrocarbons. Meanwhile, welding is a standard process in constructing oil and gas operational facilities such as transportation pipelines, production tubing, and wells. It involves connecting the carbon metallic structures by melting a filler material between the two structures at high temperatures. Once welded, the carbon steel consists of three sections: parent metal (PM), weld metal (WM), and heat-affected zone (HAZ). The PM refers to the base metal in the weld region, while the WM results from the melting that forms the fusion between the filler metal and base metal. The HAZ is the section of the weld segments that are affected due to high temperatures [3].

The dissimilarity of the metallurgical and the compositional difference between the weld and base metal causes it to experience different types of corrosion, including galvanic corrosion and intrinsic corrosion. The combined effect of these two corrosions causes the metal to undergo a focus corrosion attack in a specific location on the weldment, leading to a severe localized attack. This type of corrosion is also called preferential weldment corrosion [4]. Several factors significantly affect preferential weld corrosion, including temperature, flow conditions, water composition, pH value, organic acid, partial pressure of CO_2 , scaling effects, weld steel composition related to the parent pipe and welding procedure [4]. In an aqueous solution containing CO_2 and other forms of weak acids such as acetic acid, the corrosion rate of the weld is accelerated. This is because organic acid reduces the pH, thus increasing the bicarbonate concentration (HCO³⁻) and the H⁺ concentration. The increase in temperature also elevates the corrosion rate due to the high CO_2 rate of reaction [5].

In recent years, there has been rapid progress in the scientific exploration of corrosion mitigation strategies. One of the most practical and cost-effective methods for corrosion control in the oil and gas industry is the use of corrosion inhibitors. Corrosion inhibitors can protect the surface of metals and retard corrosion action when added to the corrosive environment, even in small concentrations [6]. It is proven in many studies that corrosion inhibitor is an effective method of mitigating corrosion and reducing corrosion rates to acceptable limits [7]. However, most studies focus on standard corrosion conditions, such as common CO₂ cases or in hydrochloric acid and sulfuric acid medium. Only a few studies investigated the application of corrosion inhibitors in highly presence organic acids with CO₂/H₂S environments [8-10]. To make it worse, the small surface area and metal surface morphology in the region of preferential weld corrosion causes organic acid corrosion to occur more likely. Hence, it has become more challenging to find corrosion inhibitors that can work effectively in these conditions. In order to address these issues, the development of more robust and highly effective corrosion inhibitors that suit these more challenging environments and weld metal segments is needed. Previous studies on preferential weld corrosion with the presence of CO₂ have revealed that few commercial corrosion inhibitors from Clariant Oil Services have proven to reduce corrosion and mitigate corrosion specifically for welded areas in the pipeline [5,11]. These commercial corrosion inhibitors were said to be suitable for welded metal application and are known as environmentally acceptable ethoxylated amine corrosion inhibitors.

Therefore, in this study, three commercial corrosion inhibitors obtained from Clariant Oil Services Malaysia and Clariant Oil Services UK were selected for investigation and characterization via FTIR and ¹³C NMR to screen and benchmark these commercial corrosion inhibitors for application in highly organic acid conditions with CO₂ environment. Then, a series of electrochemical corrosion tests were carried out to study the inhibitive performance of these three commercial corrosion inhibitors in highly organic acid conditions. These tests were conducted under specific conditions that stimulate the actual condition in the field. The visual inspection of each metal segment was also investigated. The screening via characterization will contribute to benchmarking the types of chemical compositions and functional groups in commercial corrosion inhibitors. Meanwhile, evaluating the performance of commercial corrosion inhibitors in mitigating corrosion will help benchmark the inhibition efficiency of corrosion inhibitors under CO₂ conditions with the presence of acetic acid.

2. Methodology

2.1 Screening and Benchmarking via Structure Elucidation

Three commercial corrosion inhibitors: Corrtreat 5727 (CT5727), Corrtreat 17906 (CT17906), and Dodicor 4305 (D4305), were obtained from Clariant (Malaysia) Sdn Bhd and Clariant UK Ltd was used for the screening and benchmarking process. The screening and benchmarking process of these commercial corrosion inhibitors included the characterization of the chemical compositions. The chemical compositions and functional groups will be characterized via FTIR and ¹³C NMR. The FTIR spectra were recorded using a Perkin Elmer Spectrum 65 FTIR spectrometer with Universal ATR sampling, from 10 cm⁻¹ to 4500 cm⁻¹ spectral regions. The Mestre lab software was used to analyse the presence of the functional group. Using TMS as a standard [12], proton (¹H) and carbon (¹³C) NMR spectra were recorded on a Bruker 400 MHz SB Ultra ShieldTM spectrometer. The NMR spectra obtained was analysed using the Mestre lab software [13].

2.2 Performance Evaluation via Electrochemical Measurements 2.2.1 Preparation of mild steel samples

The steel samples: a welded A333 Grade 6 carbon steel with low nickel filler were cut into coupons in a ratio for parent metal (PM), weld metal (WM), and heat affected zone (HAZ) to represent the field conditions. An insulated copper wire was attached to each metal specimen and slotted through a 200 mm length, 0.3 mm diameter of PVC tube to allow for electrical connection during the test. The specimen were later embedded within a two-component epoxy resin in a linear arrangement in a 30 mm diameter mold to produce a working electrode (WE). Each electrode was then wet-grinded with 60, 120, 240, 320 and 600 silicon carbides grit paper until reflective sides were achieved and rinsed with acetone, blow-dried, and placed in a desiccator or dry box before use.

2.2.2 Test parameters

Table 1 shows the parameters set for all tests conducted in the basic condition of 60°C, 3 wt.% of NaCl, 1.0 bar of CO₂ partial pressure, 1500 ppm of acetic acid (HAc), and 30 and 200 ppm of injected inhibitors. These parameters were set based on the actual condition applied in the field. 30 ppm of injected corrosion inhibitors stimulate pipeline crude, while 200 ppm stimulates pipeline condensate. Meanwhile, 1500 ppm of acetic acid refers to the dosage used in the PWC initiative. All three selected corrosion inhibitors have a different compositions. For CT5727, it is an aqueous solution of alkyl dimethyl benzyl ammonium chloride with colourless liquid appearance. For CT17906 is an imidazoline-type corrosion inhibitor with brown liquid appearance, and D4305 is a di/tri amine ethoxylate corrosion inhibitor with dark brown appearance. All tests were conducted in a glass cell using a three-electrode system, with stainless steel as the counter electrode and silver-silver chloride (Ag/AgCl) as the reference electrode. The working electrode consists of the PM, HAZ and WM. Before each test, the brine solution was continuously purged with CO₂ gas for at least one hour and during the test to ensure that the CO₂ saturation was achieved and maintained.

Parameter	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6		
Concentration of HAc (ppm)	0	1500	0	1500	0	1500		
Types of Inhibitors	Corrtreat 5727 (CT5727)		Corrtreat 1790)6 (CT 17906)	Dodicor 4306 (D 4306)			
Inhibitor concentrations (ppm)	0 30 200	0 30 200	0 30 200	0 30 200	0 30 200	0 0 30 200		

Table 1

2.2.3 Test setup

All tests were performed using a three-electrode configuration glass cell, with stainless steel as the counter electrode and silver-silver chloride (Ag/AgCl) as the reference electrode. The working electrode consists of the PM, HAZ and WM, as shown in Figure 1. The brine solution is fixed to 3 wt.% NaCl, heated to 60°C and purged continuously with CO₂ gas for at least one hour before and during the test to ensure that the CO₂ saturation was achieved and maintained. This is an essential step during the test to simulate the environmental condition and for the precipitation of FeCO₃ to occur. The test was then left for 2-day pre-corrosion, followed by injection of 30 ppm corrosion inhibitor on the third and 170 ppm (a total of 200 ppm) of corrosion inhibitors on the fourth day. The electrochemical measurement of each test was collected continuously with a 30-minute time interval between each measurement, using the linear polarisation resistance (LPR) technique for the measurement of intrinsic corrosion rate and the zero resistance ammeter (ZRA) technique for the measurement of galvanic corrosion rate of each metal specimen. These two measurements were then used to calculate the total corrosion rate of the metal specimens. The data acquisition was analysed using the computer connected to the ACM Instruments GalvoGill12 and the Core Running software. The test was repeated for each inhibitor with and without the addition of acetic acid (1500 ppm) to compare the corrosion rate in the presence of acetic acid.

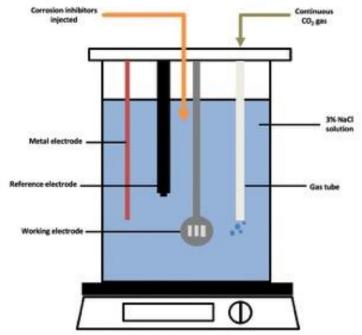


Fig. 1. Glass cell setup for electrochemical testing

3. Results and Discussions

3.1 Characterization of Commercial Corrosion Inhibitors

Table 2

In this study, three commercial corrosion inhibitors: Corrtreat 5727 (CT5727), Corrtreat 17906 (CT17906), and Dodicor 4305 (D4305), were selected as the inhibitors of interest due to their application history in the preferential weld corrosion with the presence of CO₂ [6]. All three corrosion inhibitors were characterized using FTIR and ¹³C NMR to identify the functional groups responsible for increasing the inhibition efficiency and acted as a reference for developing and modifying new corrosion inhibitors. Figure 2 shows the FTIR spectra for all commercial corrosion inhibitors. Based on the spectra, both CT5727 and CT17906 exhibit similar peaks, indicating the presence of identical functional groups such as hydroxy (O-H), alkyl (C-H), and alkene (C=C) groups. Meanwhile, inhibitor D4305 shows the occurrence of the amide group (N-H) and ether (C-O) group at the adsorption bands of 3611-3106 and 1103 cm⁻¹. Table 2 enlists the functional groups and their corresponding wavenumbers for all three inhibitors.

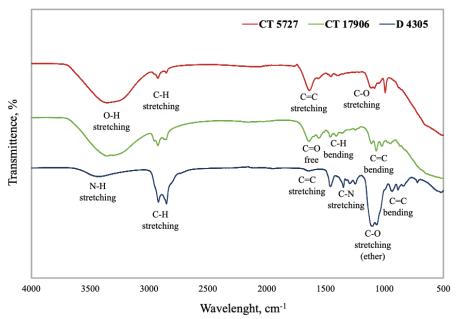
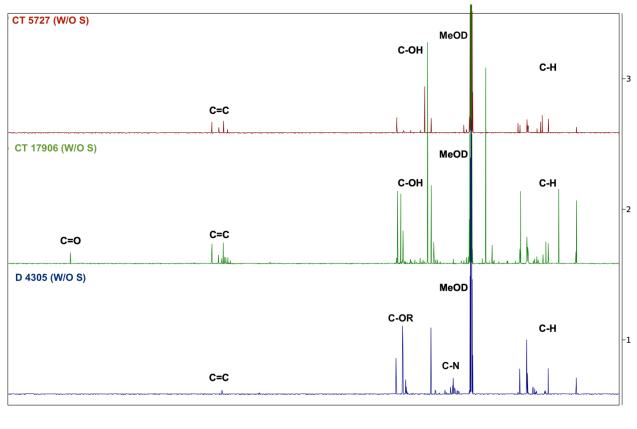


Fig. 2. FTIR spectrum for all three corrosion inhibitors

Functional group and frequency of FTIR					
IR band (cm ⁻¹)[14]		Assignment			
References	Data Obtained				
3700-3200	3660-2970	O-H stretching			
3400-3310	3611-3106	N-H stretching, secondary amide			
3000-2840	2980-2810	C-H stretching vibration			
1678-1648	1641-1637	C=C stretching, alkene			
1650	1640	C=O stretching, free associated			
1465-1450	1458-1454	C-H bending vibration			
1342-1266	1349	C-N stretching			
1210-1124	1103	C-O bending, ether			
1085-1050	1085-1070	C-O stretching			
995-885	994-936	C=C bending			

The ¹³C NMR spectra were recorded in deuterated methanol using Bruker 400 MHz SB Ultra ShieldTM. The ¹³C NMR helps to confirm the functional group present in all benchmark inhibitors. As depicted in Figure 3, the ¹³C NMR spectrum for all three inhibitors shows peaks in the region of δ 12-44 represents the carbon for primary, secondary, and tertiary alkyl groups. Similar to FTIR spectra, both CT5727 and CT17906 show almost the same functional groups present in the structure except for the presence of the carbonyl group (C=O) in CT17906 at the region of δ 180. Meanwhile, the peak at the region of δ 50-58 further confirms the presence of the amine group in the structure of inhibitor D4305. Besides, the presence of C-O carbon in D4305 is believed from the ether group while alcohol group in inhibitors CT5727 and CT17906. Overall, the FTIR and ¹³C NMR spectra conclude that all three inhibitors have few identical functional groups in their chemical structure, such as hydroxy, alkyl, and alkene groups. However, only CT17906 has the presence of carbonyl group while D4305 has amine and ether group in their structure. Table 3 enlists the functional groups and their corresponding chemical shift for all three inhibitors.



f1 (ppm) Ó Fig. 3. ¹³C NMR spectrum for all three corrosion inhibitors

Table 3		
¹³ C NMR ch	emical shift	
IR band (cm ⁻¹)[15]		Assignment
References	Data Obtained	
5-50	12-44	C-H, primary, secondary, and tertiary carbon
40-60	50-58	C-N carbon
50-100	60-75	C-O carbon
100-150	125-133	C=C
150-180	180	C=0

3.2 Performance Evaluation of Commercial Corrosion Inhibitors

The performance evaluation of commercial corrosion inhibitors using electrochemical (LPR and ZRA) measurement tests was conducted to investigate the inhibition performance and the corrosion rate of the commercial inhibitors in the presence of organic acid as a benchmark study. This study selected three inhibitors as benchmark corrosion inhibitors based on their application in the oil and gas industry with CO₂ conditions and preferential weld corrosion (PWC). All tests were conducted in the basic condition of 60°C, 3 wt.% of NaCl, 1.0 bar of CO₂ partial pressure, 1500 ppm of acetic acid (HAc), and 30 and 200 ppm of injected inhibitors. Each test (Test 1 until Test 6) was conducted for four days (96 hours) divided into 2-day pre-corrosion, also known as Blank, followed by corrosion inhibitors injection in the next two days (30 and 200 ppm). The same experiment was conducted for each inhibitor with and without the addition of HAc to compare the performance and the corrosion rate. The data analysis consisted of the linear-polarization resistance (LPR) corrosion, and the total corrosion rate for all tests. In addition, the visual surface analysis of the metals was also included before and after each test. Table 4 lists all the intrinsic, galvanic and total corrosion rates for all tested corrosion inhibitors in the absence and presence of HAc.

3.2.1 Intrinsic corrosion rate

Intrinsic corrosion is referred to the natural tendency of a metal to self-corrode or self-corrosion of the metal. This corrosion rate was measured using the linear polarization resistance (LPR) technique by connecting the working electrode (WE1) to the reference electrode (RE) and the auxiliary electrode (AE) in the glass cell. Figure 4 illustrates the trend shown by the intrinsic corrosion rate of each metal, PM, HAZ and WM, before and after the addition of corrosion inhibitor CT5727. As indicated in the graph, it appears that inhibitor CT5727 perform well in mitigated corrosion for all metal segment in both conditions. In the absence of acetic acid, the corrosion rate for PM was observed to be reduced from 0.86 mmpy during pre-corrosion to 0.036 mmpy at the maximum concentration of corrosion inhibitors injected. Similarly, the corrosion rate was also reduced for HAZ and WM, with WM showing the highest reduction from 4.73 mmpy to 0.055 mmpy. However, the presence of acetic acid has caused an increase in the corrosion rate as observed in the pre-corrosion of all metals ranging from 4.57 to 6.72 mmpy. This is due to the effect of acetic acid, which disrupted the adsorption of inhibitor molecules toward the metal surface, further accelerating the corrosion rate [16,17]. Therefore, the corrosion rate only reached 0.59 to 0.98 mmpy even after the maximum corrosion inhibitor injection.

The same trend was observed in both CT17406 and D4305, in which the corrosion rate dramatically increased with the addition of HAc in the system. However, CT17406 was proven to have better inhibitive performance in conditions with HAc among all the tested inhibitors. As tabulated in Table 4, inhibitors CT17409 have successfully reduced the corrosion rate of WM from 12.56 mmpy during the pre-corrosion to 0.81 mmpy at the maximum concentration of 200 ppm. On the other hand, inhibitors D4305 show the least effective inhibitive performance with the lowest recorded corrosion rate, only ranging from 0.72 to 3.77 mmpy for all metals segment at the maximum concentration of corrosion inhibitors. Besides, the corrosion rate for each metal was also seen to increase over time in the presence of acetic acid due to the formation of crevice corrosion in between the epoxy resin cast and the metal. Overall, all tested corrosion inhibitors show a decline in corrosion rate with the increase of inhibitors concentration from 0 ppm to 200 ppm.

Table 4

The intrinsic, galvanic and total corrosion rates for all tested corrosion inhibitors in the absence and presence of acetic acid

Corrosion	Concentration of Acetic Acid	Corrosion Inhibitors	Corrosion Rate								
Inhibitors (ppm)	Injected (ppm)	Intrinsic Corrosion Rate (mpy)			Galvanic Corrosion Rate (mA/cm²)			Total Corrosion Rate (mm/y)			
											PM
		CT5727 0	0	0	0.86	0.67	4.73	-0.07	-0.17	0.30	0.79
	30		0.08	0.16	0.19	-0.02	0.05	-0.01	0.06	0.21	0.18
		200	0.036	0.043	0.055	0.004	0.008	-0.017	0.040	0.051	0.038
1500	1500	0	4.57	6.72	4.88	-0.32	-1.92	2.41	4.25	4.80	7.29
		30	1.17	3.05	1.89	-0.21	-0.35	0.80	0.96	2.70	2.69
	200	0.59	1.60	0.98	-0.10	-0.18	0.40	0.49	1.42	1.38	
CT17406 0 1500	0	0	4.25	6.12	9.79	-0.17	-0.35	0.85	4.08	5.77	10.64
		30	0.23	0.35	2.01	-0.25	-0.38	1.19	-0.02	-0.03	3.20
		200	0.12	0.12	0.35	-0.04	-0.01	0.12	0.08	0.11	0.47
	1500	0	2.90	6.02	12.56	-0.49	-1.98	3.45	2.41	4.04	16.01
	30	0.63	1.89	2.45	-0.15	0.16	0.29	0.48	2.05	2.74	
	200	0.21	0.51	0.81	-0.08	0.05	0.19	0.13	0.56	1.00	
D4305 0 1500	0	0	5.35	6.76	10.77	-0.36	-0.44	1.55	4.99	6.32	12.32
		30	4.39	5.43	9.41	-0.35	-0.62	1.74	4.04	4.81	11.15
		200	1.16	3.26	7.76	-1.11	0.17	3.34	0.05	3.43	11.11
	1500	0	0.71	2.33	2.93	-0.17	-0.44	0.92	0.54	1.89	3.85
		30	0.63	2.40	2.99	-0.10	-0.53	0.85	0.53	1.87	3.84
		200	0.72	2.70	3.77	-0.08	-0.71	0.94	0.63	1.99	4.71

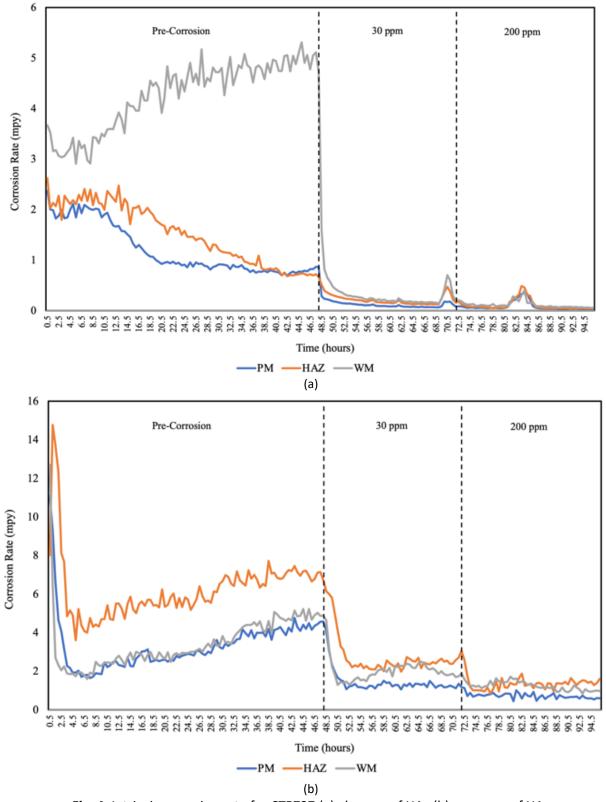


Fig. 4. Intrinsic corrosion rate for CT5727 (a) absence of HAc (b) presence of HAc

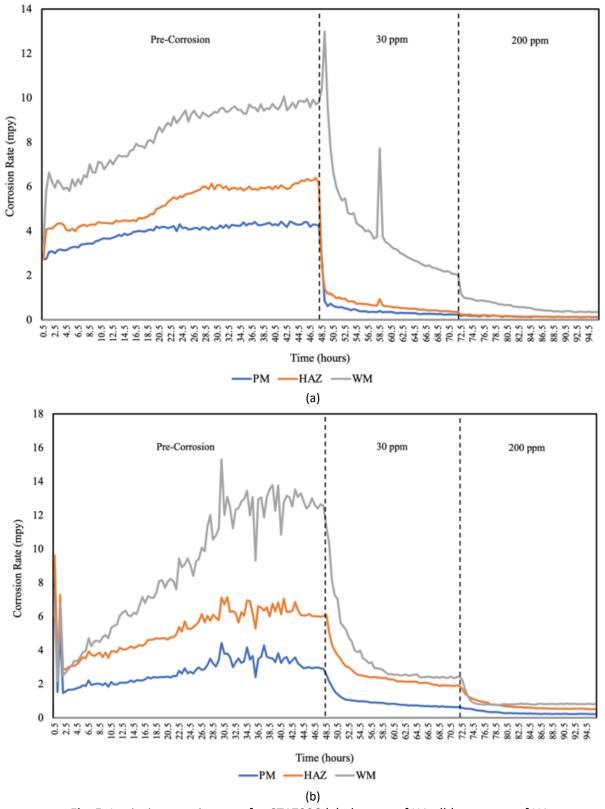


Fig. 5. Intrinsic corrosion rate for CT17906 (a) absence of HAc (b) presence of HAc

Journal of Advanced Research in Applied Mechanics Volume 102, Issue 1 (2023) 10-31

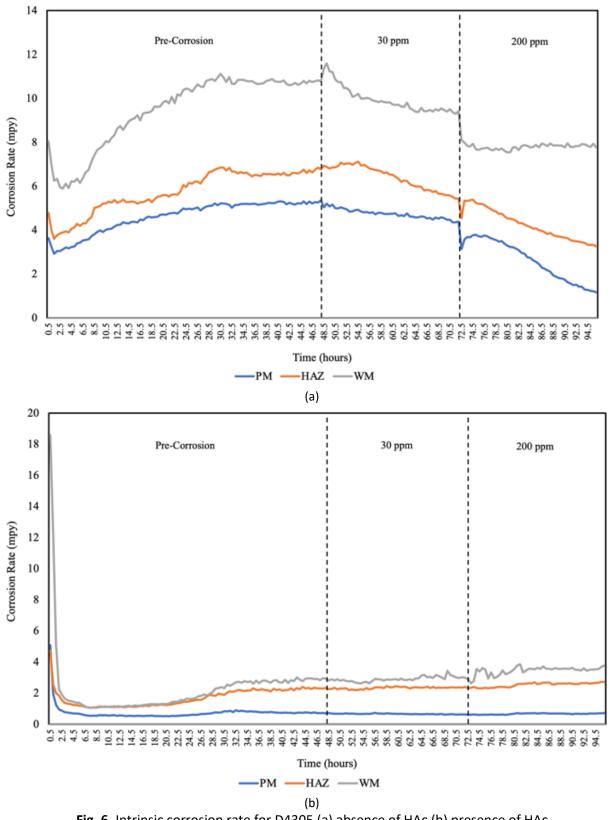


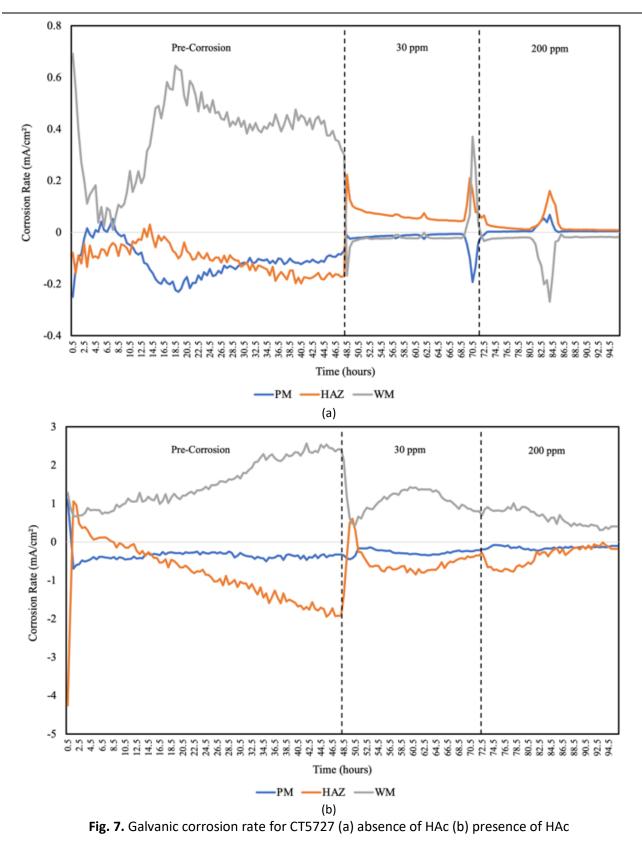
Fig. 6. Intrinsic corrosion rate for D4305 (a) absence of HAc (b) presence of HAc

3.2.2 Galvanic corrosion rate

Galvanic corrosion occurs when two or more dissimilar metals with different electrode potentials are coupled together and exposed to a corrosive environment [18]. Typically, the more active metal (anode) will tend to corrode at an accelerated rate, while the more noble metal (the cathode) will corrode at a slow rate [19]. The galvanic current behaviour for inhibitor CT5727 in the absence and presence of HAc was presented in Figure 7. It can be observed that WM was anodic to both PM and HAZ during the pre-corrosion period. These galvanic currents started to decay with the addition of inhibitor CT5727 and caused current reversal to occur, with WM becoming cathodic while PM and HAZ becoming anodic. The sharp decrease observed in the WM during the addition of inhibitors was attributed to the formation of partially protective corrosion film in the metal. It was favourable for the WM to be the cathodic component as the other weld regions provided sacrificial protection, reducing its corrosion rate [20]. However, in the presence of HAc, all the metals were anodic during the initial of the pre-corrosion period and started to decay and cause both PM and HAZ to become cathodic, while WM maintained its anodic behaviour and protected the PM and HAZ metal until the end of reactions. Figure 8 illustrates the galvanic current behaviour of the metals for the system with the addition of inhibitor CT17906. In the absence of HAc, the galvanic behaviour of the metal was consistent throughout the test, with WM having an anodic current. At the same time, both PM and HAZ were cathodic. Meanwhile, in the system with HAc, it is apparent that both PM and HAZ show anodic behaviour during the first one hour of pre-corrosion for PM and first 13 hours for HAZ metal and then overturned to become cathodic throughout the pre-corrosion period. After inhibition, another reversible rise in the current of HAZ occurred and causing it to become slightly anodic, while PM maintains as cathodic. At the same time, the WM undergoes a reduction of galvanic currents for every addition of inhibitors but overall maintains its anodic behaviour throughout the test.

Finally, the galvanic behaviour for the test with inhibitors D4305 was presented in Figure 9. Both conditions show a similar trend for all three metals as in the galvanic behaviour for inhibitor CT17906 (Figure 8). Weld metal shows consistent anodic galvanic behaviour similar to CT17906, while both PM and HAZ acted as cathodic, except for the sudden rise of galvanic behaviour of HAZ metal during the final addition of inhibitor, which resulted in the changing of HAZ galvanic behaviour to anodic. Likewise, the trend of galvanic behaviour in the presence of HAc was similar to in Figure 8. Both PM and HAZ show anodic behaviour during the early period of pre-corrosion and reversed to become cathodic throughout the test and vice versa to WM. All in all, the galvanic behaviour of all metals in all systems was consistent for all tests. The difference in the galvanic current was associated with the different compositions of the PM, HAZ and WM. However, it can be seen in the trend of galvanic current measurement, as evidenced in Table 4, that the galvanic current mainly was found to approach zero, thus demonstrating that galvanic interaction was only had a small contribution to the corrosion process [21]. It is intrinsic corrosion that is responsible for the corrosion that occurred in each test.

Journal of Advanced Research in Applied Mechanics Volume 102, Issue 1 (2023) 10-31



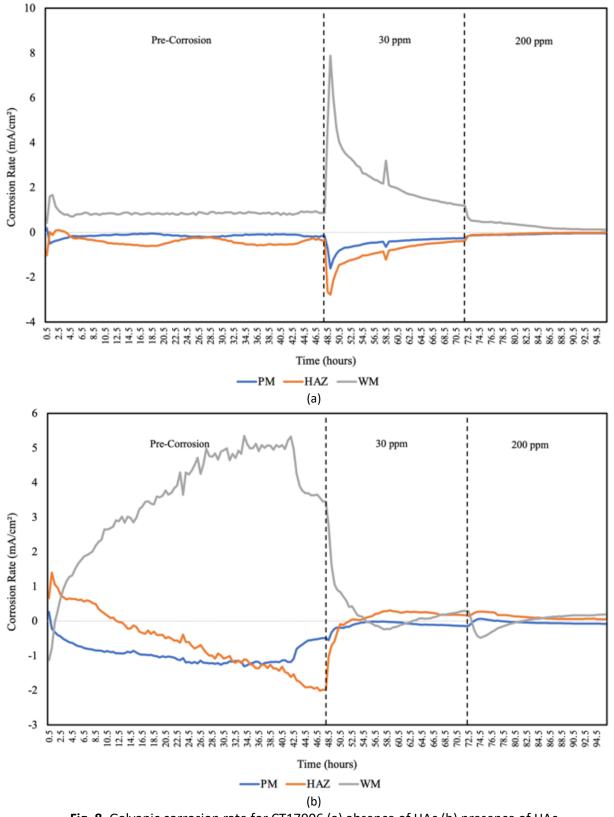
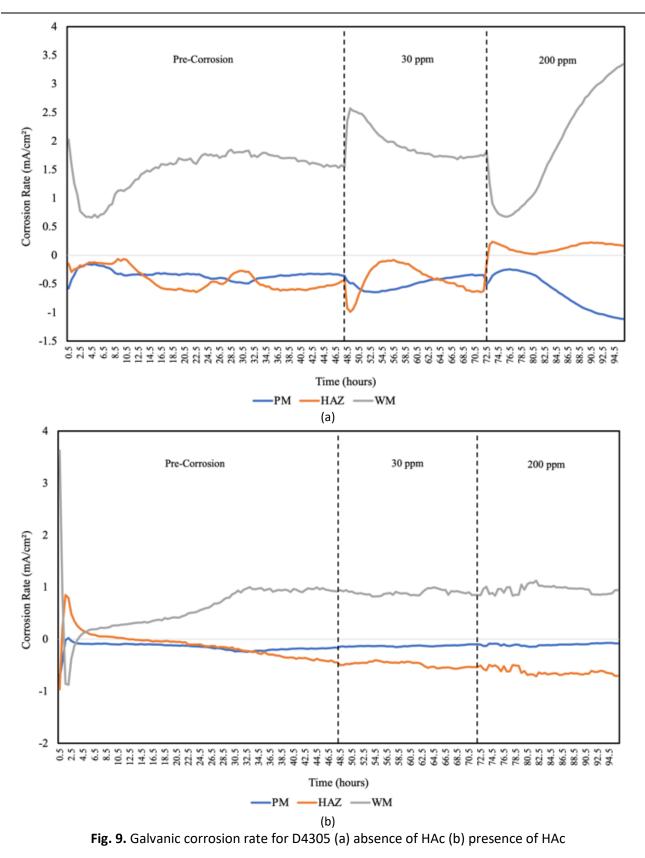


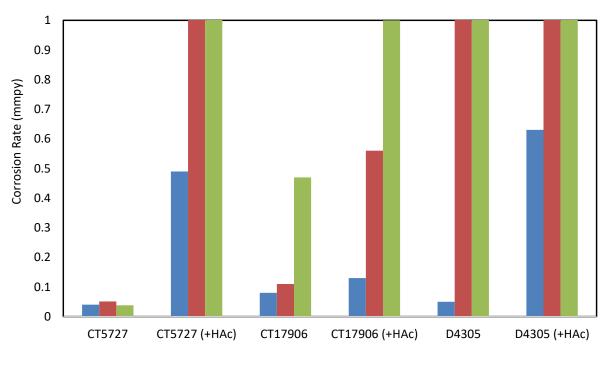
Fig. 8. Galvanic corrosion rate for CT17906 (a) absence of HAc (b) presence of HAc



3.2.3 Total corrosion rate

The total corrosion rate of each metal was calculated from the sum of its intrinsic and galvanic corrosion rates [22]. In this study, the effect of galvanic corrosion rates is too small for each metal

sample to cause galvanic type preferential corrosion. Thus, the total corrosion rate mainly relies on the intrinsic corrosion of the metal. Figure 10 shows the total corrosion rate for all systems at the maximum concentration (200 ppm) of corrosion inhibitors. While Figures 11-13 present the total corrosion rate for each system in all concentrations of inhibitors. As indicated in the graph, it was revealed that only one inhibitor achieved a total corrosion rate below the acceptable limit of 0.1 mmpy, while the others were above 0.1 mmpy. Corrosion inhibitor CT5727 has the highest inhibition performance with the lowest corrosion rate of 0.040, 0.051 and 0.038 mmpy for PM, HAZ and WM, respectively. However, the performance of CT5727 showed a decline with the addition of HAc into the system. The presence of HAc has disrupted the adsorption of inhibitors molecules and lowered the inhibitive performance of CT5727. Thus, resulting in a slightly higher corrosion rate of 0.49, 1.42 and 1.38 mmpy for PM, HAZ and WM, respectively. On the other hand, inhibitor CT17906 shows promising results in its inhibitive activities in both systems with and without acetic acid, even though the overall total corrosion rate does not meet the acceptable limit of corrosion rate per year. In this case, the protection layers are still being formed in PM and HAZ metal, which is associated with the lower corrosion rate of PM and HAZ in the system. However, the low resistance of WM toward corrosion has failed CT17906 in protecting the metal from undergoing corrosion. Meanwhile, inhibitor D4706 has proven to be the least effective inhibitor, with a total corrosion rate of 11.11 and 4.71 mmpy for WM in both systems.



PM HAZ WM

Fig. 10. Total corrosion rate for all systems at the maximum concentration of inhibitors

Journal of Advanced Research in Applied Mechanics Volume 102, Issue 1 (2023) 10-31

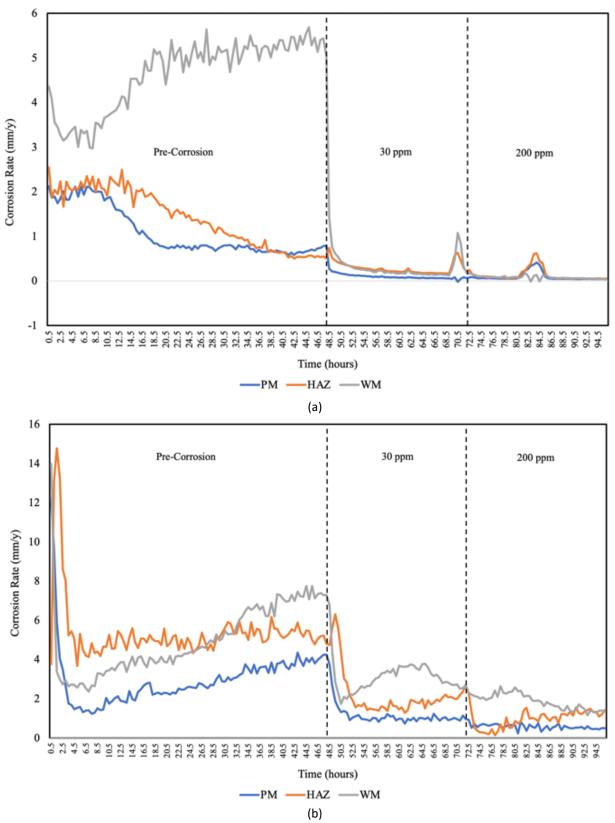


Fig. 11. Total corrosion rate for CT5727 (a) absence of HAc (b) presence of HAc

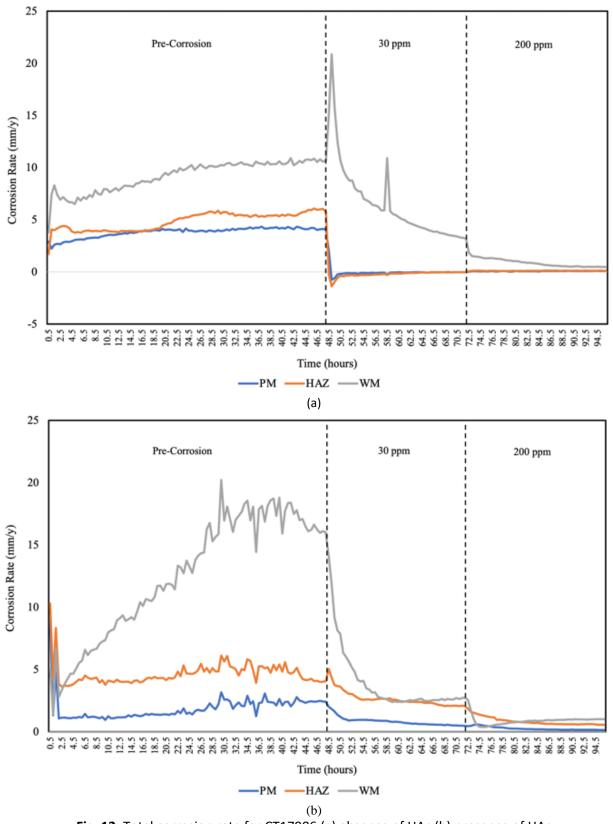


Fig. 12. Total corrosion rate for CT17906 (a) absence of HAc (b) presence of HAc

Journal of Advanced Research in Applied Mechanics Volume 102, Issue 1 (2023) 10-31

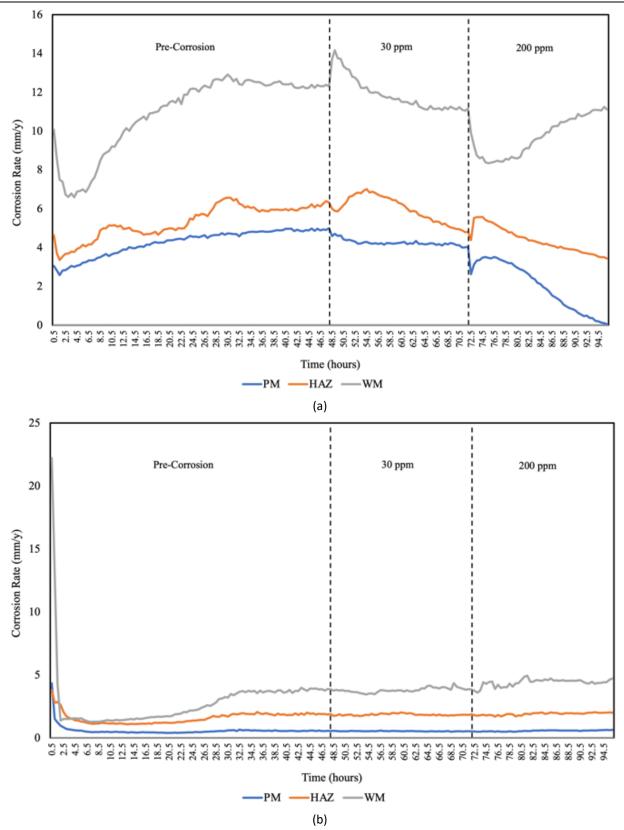
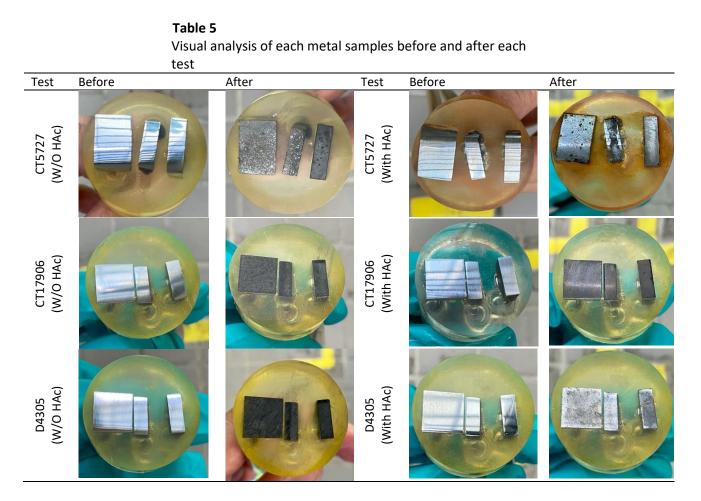


Fig. 13. Total corrosion rate for D4305 (a) absence of HAc (b) presence of HAc

3.2.4 Surface analysis

The surface analysis of each test in all systems was conducted via visual observation. All metal sample was analyse before and after each test to observe the effect of corrosion on the metal samples. Table 5 summarizes the visual analysis of each metal sample before and after each test. Prior to the test, a shiny and uniform surface was observed in each metal sample due to the grinding process. However, it can be seen clearly that each metal sample undergoes corrosion after each test due to the existence of a dark grey layer which indicates CO₂ corrosion [23-25]. A darker layer was found in each metal segment, which indicated greater corrosion products produced for the condition with HAc [26]. The presence of HAc in the system has caused more formation of the FeCO₃ layer [3], which accumulates on the metal surface, especially in HAZ and WM. This justifies the higher corrosion rate of HAZ and WM, as discussed early. Besides that, the anodic galvanic effect of WM to the PM and HAZ metal in each test has resulted in more localized corrosion occurring on the surface of WM [27]. Overall, more severe corrosion was observed in the condition with the presence of HAc, with PM having the least corrosion layers than the others.



4. Conclusions

In conclusion, all three commercial corrosion inhibitors were successfully characterized to study the functional group present in compounds and become the benchmark inhibitor for corrosion mitigation in CO_2 and organic acid conditions. It is revealed that these three inhibitors have the presence of identical functional groups, such as the alkyl (C-H) and alkene (C=C) groups. Both

inhibitors CT5727 and CT17906 have a hydroxy (O-H) group presence, but only CT17906 has the presence of carbonyl (C=O) in its compound. Meanwhile, D4305 has amine and ether groups found in its structure. The presence of these functional groups on inhibitor compounds plays an important role in corrosion inhibition performance and affecting the corrosion rate. To prove this, the performance evaluation on these three inhibitors was performed. Based on the study of the performance via electrochemical measurement, it is found that inhibitor CT17906 has the highest inhibition performance in the CO₂ environment with the presence of acetic acid, followed by CT5727 and, finally, D4305 with the worst performance. Therefore, CT17906 is the best benchmark inhibitor based on this study, with inhibition efficiency of more than 90% in both conditions with and without the presence of organic acid, even though the total corrosion rate indicated that CT17906 were unable to give a lower corrosion rate than the acceptable limit of corrosion per year. From that, we can also conclude that the carbonyl group in CT17906 provides a mitigation effect for CT17906 and increases its ability to reduce the corrosion rate compared to the other inhibitors. These screening and benchmarking studies via characterization and electrochemical measurement could be used as a future reference for the new development of corrosion inhibitors in a similar field.

Acknowledgement

This work was financially supported by PETRONAS Research Sdn Bhd and Universiti Teknologi PETRONAS (GR&T UTP) Collaboration (Grant Number 015MD0-085).

References

- [1] Popoola, Lekan Taofeek, Alhaji Shehu Grema, Ganiyu Kayode Latinwo, Babagana Gutti, and Adebori Saheed Balogun. "Corrosion problems during oil and gas production and its mitigation." *International Journal of Industrial Chemistry* 4 (2013): 1-15. <u>https://doi.org/10.1186/2228-5547-4-35</u>
- [2] Zhao, Weimin, Timing Zhang, Yonglin Wang, Jianhua Qiao, and Zerui Wang. "Corrosion failure mechanism of associated gas transmission pipeline." *Materials* 11, no. 10 (2018): 1935. <u>https://doi.org/10.3390/ma11101935</u>
- [3] Raman, T. J. "Study of Preferential Weld Corrosion in X52 Mild Steel with the Presence of Acetic Acid." Bachelor of Mechanical Engineering Dissertation Universiti Teknologi PETRONAS, Tronoh, Perak. (2016).
- [4] Huang, Lei, Bruce Brown, and Srdjan Nesic. "Investigation of environmental effects on intrinsic and galvanic corrosion of mild steel weldment in CO2 environment." In *Corrosion 2014*. OnePetro, 2014.
- [5] Adegbite, M. A. "Flow Accelerated Preferential Weld Corrosion of X65 Steel in Brine Containing Carbon Dioxide and Oxygen." Cranfield University: Doctoral Dissertation, School of Applied Sciences. (2014).
- [6] West, John Michael. "Basic corrosion and oxidation." Halsted Press (1986).
- [7] Papavinasam, S. "Corrosion Inhibitors" in Uhlig's Corrosion Handbook, Second Edition, John Wiley & Sons Inc. Page 1089-1105 (2000).
- [8] Honda, Hiroshi, Toshiyuki Sunaba, Yasuyoshi Tomoe, Tomoko Watanabe, and Martin Foss. "Corrosion Behaviors of CRAs Under CO2-H2S Environment with Organic Acids." In *Corrosion 2012*. OnePetro, 2012.
- [9] Ayyagari, Sahithi, Maryam Eslami, Bruce Brown, and Srdjan Nesic. "Corrosion Mechanisms of Mild Steel in the Presence of Formic Acid and Acetic Acid." In *AMPP Annual Conference+ Expo*. OnePetro, 2022.
- [10] Talukdar, Anusuya, and Prasanna Venkatesh Rajaraman. "Effect of acetic acid in CO2-H2S corrosion of carbon steelatelevatedtemperature." MaterialsToday:Proceedings 57(2022):1842-1845.https://doi.org/10.1016/j.matpr.2022.01.036
- [11] Alawadhi, Khaled, M. Robinson, A. Chalmers, and I. G. Winning. "Inhibition of weld corrosion in flowing brines containing carbon dioxide." In *CORROSION 2008*. OnePetro, 2008.
- [12] Hoffman, Roy E. "Standardization of chemical shifts of TMS and solvent signals in NMR solvents." Magnetic Resonance in Chemistry 44, no. 6 (2006): 606-616. <u>https://doi.org/10.1002/mrc.1801</u>
- [13] Willcott, M. R. "MestRe Nova" Journal of Americam Chemical Society 131, no. 36: 13180 (2009). <u>https://doi.org/10.1021/ja906709t</u>
- [14] IR Spectrum Table & Chart, Merck KGaA, (2021). [Online]. Available: https://www.sigmaaldrich.com/MY/en/technical-documents/technical-article/analytical-chemistry/photometryand-reflectometry/ir-spectrum-table. [Accessed 28 September 2021].

- [15] 13C NMR Chemical Shift Value, [Online]. Available: https://www.chemistrysteps.com/wpcontent/uploads/2020/02/13C-Carbon-NMR-Chemical-Shift-Values.png. [Accessed 20 September 2021].
- [16] Kahyarian, Aria, Mohsen Achour, and Srdjan Nesic. "CO2 corrosion of mild steel." *Trends in Oil and Gas Corrosion Research and Technologies* (2017): 149-190. <u>https://doi.org/10.1016/B978-0-08-101105-8.00007-3</u>
- [17] Kaewpradap, Ussama. "Validation of Top of the Line Corrosion Prediction Model Using Laboratory and Field Measurements." PhD diss., Ohio University, 2012.
- [18] Cragnolino, Gustavo A. "Corrosion fundamentals and characterization techniques." In *Techniques for corrosion monitoring*, pp. 7-42. Woodhead Publishing, 2021. <u>https://doi.org/10.1016/B978-0-08-103003-5.00002-3</u>
- [19] Palit, Sukanchan. "Recent advances in corrosion science: a critical overview and a deep comprehension." *Direct Synthesis of Metal Complexes* (2018): 379-411. <u>https://doi.org/10.1016/B978-0-12-811061-4.00011-6</u>
- [20] Martinez, M., K. Alawadhi, M. Robinson, G. Nelson, and A. MacDonald. "Control of preferential weld corrosion of X65 pipeline steel in flowing brines containing carbon dioxide." In *Corrosion 2011*. OnePetro, 2011. <u>https://doi.org/10.1179/147842210X12695149033891</u>
- [21] McNaughtan, D., and I. G. Winning. "Comparison of segmented weld corrosion tests with short and long precorrosion and the influence of synergist in corrosion inhibitors." In SPE International Symposium on Oilfield Corrosion. OnePetro, 2004. <u>https://doi.org/10.2118/87553-MS</u>
- [22] Zhang, G. X. Chapter 10 Galvanic Corrosion: Uhlig's Corrosion Handbook, Third Edition, John Wiley & Sons, Inc. Page 123-143 (2011).
- [23] Gui-rong, Yang, Song Wen-ming, Wang Fu-qiang, Ma Ying, and Hao Yuan. "The corrosion behavior in CO2 medium of 20# steel under the (CO2/aqueous solution) gas-liquid two-phase stratified flow condition." *Materials Research Express* 6, no. 1 (2018): 016534. <u>https://doi.org/10.1088/2053-1591/aae667</u>
- [24] Ochoa, Nathalie, Carlos Vega, Nadine Pébère, Jacques Lacaze, and Joaquín L. Brito. "CO2 corrosion resistance of carbon steel in relation with microstructure changes." *Materials Chemistry and Physics* 156 (2015): 198-205. <u>https://doi.org/10.1016/j.matchemphys.2015.02.047</u>
- [25] Yang, Yang, Bruce Brown, and Srdjan Nesic. "Electrochemical investigation of localized CO2 corrosion on mild steel." In *Corrosion 2007*. OnePetro, (2007).
- [26] Zhang, Hanlu, Wenqiang Huang, Han Wei, Zilong Chen, Jingyi Cao, Yuming Tang, Xuhui Zhao, and Yu Zuo. "Effect of HAc on the metastable pitting corrosion of 304 SS in NaCl solution." *Materials* 15, no. 10 (2022): 3618. <u>https://doi.org/10.3390/ma15103618</u>
- [27] M. Septhon, P. Christian Pistorious. "Localized Corrosion of Carbon Steel Weldments." Corrosion 56, no. 12, 2000). https://doi.org/10.5006/1.3280516