

# Kinetics of CO<sub>2</sub> Corrosion with Acetic Acid in Turbulent Flow Conditions

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## Abstract

CO<sub>2</sub> corrosion is the main cause of failure in upstream sector of oil and gas industry. Interactions of corrosive species, such as acetic acid (HAc), and operating conditions such as flow could influence CO<sub>2</sub> corrosion kinetics. The scope of the study is to understand the effect of small concentrations of acetic acid at turbulent flow conditions on CO<sub>2</sub> corrosion kinetics. The electrochemical study of Linear Polarization Resistance (LPR) was done using Rotating Cylinder Electrode (RCE) with various HAc concentrations at fixed pH values and different temperatures. LPR tests showed that corrosion rate increases with HAc concentration and flow velocity. Moreover, effect of HAc is more pronounced at lower speed. Thus, with the presence of low concentrations of acetic acid there seems flow dependent and flow independent that contribute to corrosion rate. Acetic acid increases corrosion rate by extra cathodic reaction which generated from dissociation and direct reduction of acetic acid.

**Key words:** CO<sub>2</sub> corrosion, acetic acid, Linear Polarization Resistance (LPR), turbulent flow.

## INTRODUCTION

Corrosivity in oil and gas pipelines and the associated equipment originates from the composition of gas and crude oil sources such as carbon dioxide, hydrogen sulfide, and organic acids. The corrosivity is also influenced by other factors, such as flow rate, pH and material characteristic. The combined effect of these factors

produce aggressive environment which results in increasing corrosion rate. At this situation, the survival of carbon steel as linepipes is not guaranteed.

Carbon steel linepipes have advantages in terms of availability, cost, and ease of fabrication over other alloys. Unfortunately, carbon steel has lower resistance to carbon dioxide corrosion. Thus, the challenge in CO<sub>2</sub> corrosion research is to understand the limit of the use of carbon steel linepipe with the motivation of possible huge economic savings.

Carbon dioxide (CO<sub>2</sub>) corrosion in the presence of HAc has been the subject of numerous studies. It is known that HAc can significantly increase CO<sub>2</sub> corrosion rate at low pH. The corrosion rates will be greater when flow takes part in the environment. Flow increases corrosion rates by increasing the mass transfer of corrosion species and/or by damaging protective film in the steel surface. Since almost flow in the field is turbulent, it is important to study CO<sub>2</sub> corrosion behavior in turbulent flow conditions.

Some experiments had been conducted to study the combined effect of acetic acid and CO<sub>2</sub> corrosion either in static conditions or in dynamic conditions. Crolet J.L [2], Mendoza, Turgoose [3], Yuhua Sun, et al [4], George [5,6], Moreira et al [7], Martinez et.al [8], Nafday [1, 9], Ismail [10] and Gudbansen, Bikolva [11]. However, most of the works was done at HAc concentration more than 100 ppm. Not much work is done at lower concentration of HAc in the range of 0 – 100 ppm. This gap is important since most of the study assumes linear correlation in the lower concentration range. The analysis will be more convincing if the interval of HAc concentration is not too large such that more information will be obtained from the missing value in the interval.

Even though there are many extensive CO<sub>2</sub> corrosion studies, the mechanism of CO<sub>2</sub> corrosion with the presence of HAc is still not clear [12]. Little information of the mechanism indirectly influences failure in the field. One of the examples is pipeline failure in Wytch Farm oilfield. The pipeline was commissioned in 1990. In 1997, one of the Wytch farm production pipelines failed due to internal corrosion. After repair, the pipeline was returned to service but failed again, almost immediately. Paisley, Bauret and Willson [13] did investigation based on data from the field. The Wytch farm produced water is unique for oilfield brines. It is containing only 40 ppm of bicarbonate (HCO<sub>3</sub><sup>-</sup>), rather than commonly which has range of 500 – 2500 ppm. This, together with a high concentration of acetate (CH<sub>3</sub>COO<sup>-</sup>) at 100 ppm resulted in a relatively of low pH of 4.5, thereby increasing the CO<sub>2</sub> corrosion rate. To support this hypothesis, they did experiment on the

laboratory and the corrosion rate observed agreed well with that predicted from the failure rate and BP corrosion rate prediction model.

Therefore, it is important to understand about the effect of HAc on CO<sub>2</sub> corrosion. This is important so that the correct material selection and corrosion mitigation method which is crucial to withstand the design live can be implemented. This is not only relevant to safety but also to cost, by avoiding under design and avoidance of over design.

## EXPERIMENTAL DETAILS

### Introduction

Electrochemical studies were performed under static and dynamic conditions with the use of Rotating Cylinder Electrode (RCE) apparatus. Linear Polarization Resistance (LPR) was employed in this research. Reproducibility of the results is ensured by accurate preparation of test samples and test solution.

### Electrochemical Test Methods

#### Linear Polarization Resistance (LPR)

This method is based on the linear approximation of the polarization behavior at potentials near the corrosion potential. Resistance polarization (Rp) is given by Stern and Geary [14] equation

$$R_p = \frac{\Delta E}{\Delta I} = \frac{\beta_A \beta_C}{(\beta_A + \beta_C) i_{corr}}$$

$$i_{corr} = \frac{B}{R_p} \text{ Where } B = \frac{\beta_A \beta_C}{(\beta_A + \beta_C)}$$

$$ba = 2.3\beta_A \text{ and } bc = 2.3\beta_C; B = babc / 2.3(ba + bc)$$

The corrosion current can be related directly to the corrosion rate from Faraday's law:

$$CR(mm/year) = \frac{315Zi_{corr}}{\rho nF}$$

Where,

- CR = Corrosion Rate (mm/year)  
 $i_{corr}$  = Corrosion current density,  $\mu A$   
 $\rho$  = Density of iron,  $7.8 \text{ g/cm}^3$   
F = Faraday's constant, 96.500 C/mole  
Z = Atomic weight (g/mol)  
n = number of exchanged electron

## Equipment

Experiments were conducted at atmospheric pressure in a glass cell. A three electrode set-up was used in all polarization experiments: a mild steel was used as the working electrode; a platinum served as the counter electrode and a saturated calomel electrode (SCE) is served as reference electrode.

## Materials

Experiments under static and turbulent conditions were conducted with mild steel (BS 970: 080A15) with the following composition:

Table 1.

Composition of steel 080A15, (BS 970)

C	(%)	0.148	Cr	(%)	0.069
Si	(%)	0.175	Mo	(%)	0.014
Mn	(%)	0.799	Ni	(%)	0.065
P	(%)	0.01	Fe	(%)	Balance
S	(%)	0.032			

## EXPERIMENTAL SET-UP

A schematic diagram of the set-up for RCE experiments is shown in Figure 1 and Figure 2.

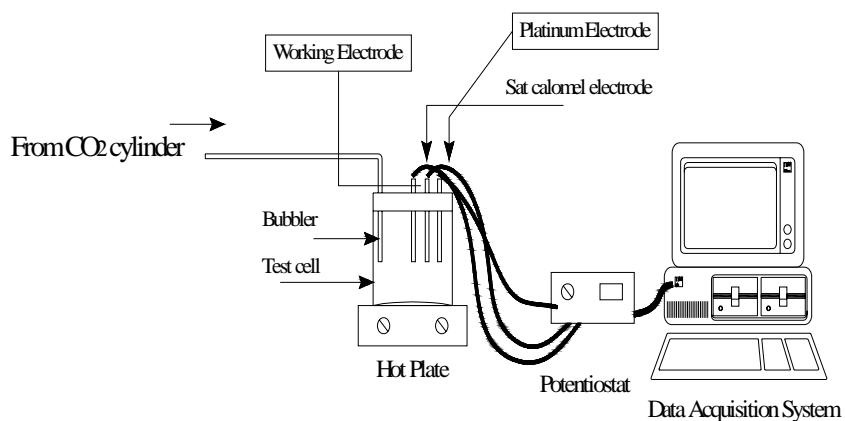


Figure. 1: Experimental set-up for LPR

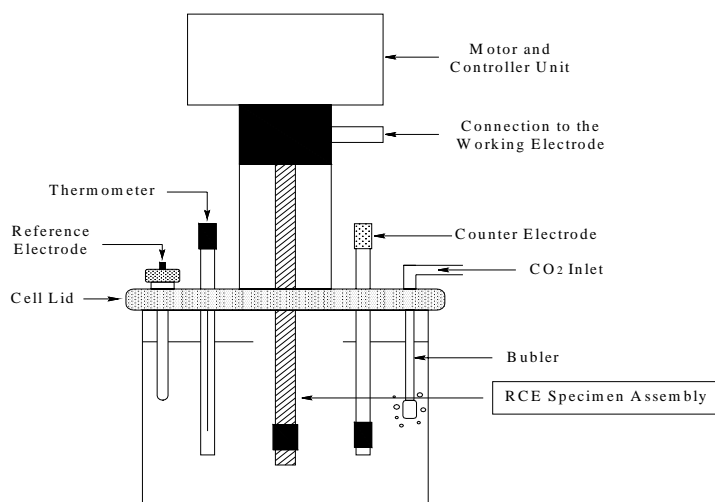


Figure 2: Detail of RCE test set-up

## TEST ENVIRONMENT

### Solution

The solutions were prepared from the following analytical reagent grade chemicals, namely glacial acetic acid (HAc), sodium acetate (NaAc), and sodium bicarbonate (NaHCO<sub>3</sub>).

Chemicals/Solvents	Specification
Deionised water	Elga Powerlab Option
Sodium Chloride	Fisher Scientific, 99%
Glacial Acetic Acid	Fisher Scientific, 100%
Sodium acetate anhydrous	Fisher Scientific, 99%
CO <sub>2</sub>	MDX, 99.8%
Sodium Bicarbonate	Fisher Scientific

The 3% NaCl solution is saturated with CO<sub>2</sub> by purging for one hour prior to the exposure of electrode. The pH of the solution could be adjusted by adding an amount of 1M NaHCO<sub>3</sub>. The pH value is checked by microcomputer pH-meter from METTLER-TOLEDO Instruments.

### Addition of Acetic Acid and Acetate

The amount acetic acid/acetate that will be added is determined by the Handerson-Hasselbach equation ( $\text{pH} = \text{pK}_a + \log_{10}[\text{Base}]/[\text{Acid}]$ ).

For acetic acid buffer, the equation is:

$$\text{pH} = 4.76 + \log_{10} [\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}]$$

The ratio of acetate ions and acetic acid at pH 6 is shown in the Table 2.

Table 2: Calculated ratio of base and acid

pH Value	Ratio	
	[CH <sub>3</sub> COO <sup>-</sup> ]	[CH <sub>3</sub> COOH]
6	17	1

## TEST MATRIX

The test matrix in the Table 3 was performed in this study.

Table 3.

Test matrix of the research

Parameter	Value
Steel type	Mild Steel, BS-970
Solution	3 % NaCl
Gas	CO <sub>2</sub>
pH	6
Total HAc (ppm)	0 (Blank Solution), 10, 20, 40, 60
Temperature (°C)	25,40,60
Rotational Velocity (rpm)	1000,2000,4000,6000
Sand paper grit used	180, 320, 600
Measurement techniques	LPR

## EXPERIMENTAL PROCEDURE

### Linear Polarization Resistance (LPR) Measurements

The LPR procedure for the test is conducted after CO<sub>2</sub> gas bubbling for one hour, adjusting the solution to the required pH and attaining the set temperature. The bubbling is reduced and maintained throughout the test.

1. Bubble CO<sub>2</sub> through the 1-litre 3% NaCl for 1 hour before inserting sample.
2. Adjust pH to the required values by adding solution of 1M NaHCO<sub>3</sub>. pH is measured at room temperature by pH meter.
3. Set the temperature and maintain with accuracy about 5°C.
4. Add the mixture of HAc and Ac accordingly to the required pH values.
5. Insert the polished specimen.
6. Adjust the rpm to the required value.
7. Set the scan rate 10 mV/minute.
8. Take readings every 15 minutes for at least 3 hours.

## RESULTS AND DISCUSSIONS

The average corrosion rates of carbon steel exposed to various concentration of HAc at pH 6 and temperature of 25, 40 and 60°C with various rotational rates are shown in Table 4 below and Figures 3–5 in the Appendix.

Table 4.

Average corrosion rates at pH 6, temperature 25°C, 40°C and 60°C with various HAc concentrations and rotational rates

[HAc]	Temperature (°C)	Average Corrosion Rates of Different Rotation Speeds (mm/yr)				
		0 rpm	1000 rpm	2000 rpm	4000 rpm	6000 rpm
Blank Solution (0 ppm)	25°C	0.679	0.91	1.19	1.28	1.46
	40°C	0.9	1.09	1.94	2.03	2.1
	60°C	1.64	1.94	2.19	3.4	3.6
10 ppm	25°C	1.106	1.2	1.37	1.42	1.53
	40°C	1.257	1.91	2.08	2.23	2.84
	60°C	1.8	1.98	3.47	3.54	4.08
20 ppm	25°C	1.2	1.32	1.4	1.47	1.6
	40°C	1.68	2.01	2.2	2.82	2.93
	60°C	2.07	2.48	3.54	3.65	4.1
40 ppm	25°C	1.235	1.41	1.46	1.49	1.69
	40°C	2.03	2.09	2.48	2.88	3
	60°C	2.1	2.52	3.63	3.85	4.23
60 ppm	25°C	1.46	1.64	1.75	1.89	2.02
	40°C	2.24	2.47	2.8	2.95	3.1
	60°C	2.43	2.7	3.85	4.2	4.48

It is seen from Table 4 that corrosion rate is influenced by HAc concentrations, velocity and temperature. Thus, the discussions of the study are divided in terms of effect of HAc concentrations, velocity and temperature.



## Effect of HAc concentrations

### Effect of HAc concentrations at 25°C

It is found that the addition of HAc species into the solution increase the corrosion rates as compared to the blank solution. The results are shown in Table 7.

Table 7.

Percentage increase in corrosion rates with the increase in HAc concentration at pH 6, 25°C.

Rotation speed (rpm)	Blank solution (mm/yr)	Percentage difference corrosion rates compared to the blank solution			
		10 ppm	20 ppm	40 ppm	60 ppm
1000	0.91	32 %	45 %	55 %	80 %
2000	1.19	15 %	18 %	23 %	47 %
4000	1.28	11 %	15 %	16 %	48 %
6000	1.46	5 %	10 %	16 %	38 %

It is observed that no significant effect of HAc at velocity 2000, 4000 and 6000 rpm for addition less than 60 ppm HAc. Corrosion rate rises from 5 % – 23 % as compared to the blank solution. On contrary, a significant effect of HAc was found at 1000 rpm. An increment of corrosion rate from 32 % – 80 % is recorded. Generally, corrosion rates increase with increasing HAc concentrations. The highest corrosion rates occur at 60 ppm HAc. This is true for all rotation speeds.

### Effect of HAc concentrations at 40°C

Similar trend is found at temperature 40°C. The significant effect of HAc occurs at 1000 rpm. An increment of corrosion rate is seen from 75 % – 127 %. At higher speed, the effect of HAc becomes minor. The maximum corrosion rates, approximately 45 %, are registered at 60 ppm HAc. The results are shown in Table 8 below.

Table 8.

Percentage increase in corrosion rates with the increase in HAc concentration at pH 6, 40°C.

Rotation speed (rpm)	Blank solution (mm/yr)	Percentage difference corrosion rates compared to the blank solution			
		10 ppm	20 ppm	40 ppm	60 ppm
1000	1.09	75 %	84 %	92 %	127 %
2000	1.11	7 %	13 %	29 %	44 %
4000	2.03	10 %	39 %	42 %	45 %
6000	2.1	35 %	40 %	43 %	48 %

### Effect of HAc concentrations at 60°C

The different behavior is observed at temperature 60°C. The additions of HAc species have major effect in increasing corrosion rates at 2000 rpm. HAc increases corrosion rates from 58 % – 76 % as compared to the blank solution. The results are shown in Table 9 below.

Table 9.

Percentage increase in corrosion rates with the increase in HAc concentration at pH 6, 60°C.

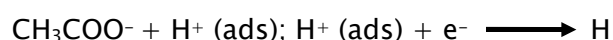
Rotation speed (rpm)	Blank solution (mm/yr)	Percentage difference corrosion rates compared to the blank solution			
		10 ppm	20 ppm	40 ppm	60 ppm
1000	1.94	2 %	28 %	30 %	39 %
2000	2.19	58 %	62 %	66 %	76 %
4000	3.4	4 %	7 %	13 %	24 %
6000	3.6	13 %	14 %	18 %	24 %

As seen from the results above, it is observed that at temperature 25°C, 40°C and 60°C, corrosion rates increase with increasing HAc concentrations. Furthermore, it is

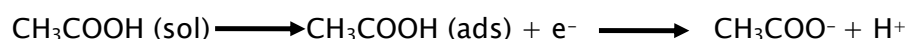
worthy note that the effect of HAC is significant at low speed, which are 1000 rpm for temperature 25°C, 40°C and 2000 rpm at 60°C.

In general, HAC increases corrosion rates by extra cathodic reaction. The extra cathodic reactions are from extra source of hydrogen ions (H<sup>+</sup>) from dissociation and direct reduction of acetic acid on the electrode surface. The sequence was proposed by Crolet [15]:

Dissociation of acetic acid



Direct reduction of undissociated acetic acid molecules



Since the dissociation of acetic acid is fast [16], it is difficult to distinguish the above two reactions.

## Effect of Rotational Speed

The effect of rotation speeds at different temperature with various HAC concentrations from 0 ppm – 60 ppm are shown in Figure 6– 8 in the Appendix. As discussed above, the effect of HAC is more pronounced at low rotation speed, approximately 1000 – 2000 rpm as compared to higher speed. Thus, it can be concluded that mechanism corrosion is influenced by mass transfer lower speed, while at high speed, it is by activation control.

Mokhtar [10] and George [5,6] concluded that there are flow independent (activation control) and flow dependent (mass transfer control) to limiting current (i<sub>lim</sub>) which responsible in increasing corrosion rate. The flow dependent is due to the reduction of H<sup>+</sup>, H<sub>2</sub>CO<sub>3</sub> and HAC. On contrary, Guldbrandsen concluded that the flow dependent is due to the reduction of H<sup>+</sup>, H<sub>2</sub>CO<sub>3</sub> only.

Another opinion comes from Schmitt [12]. He concluded that flow has responsible in bring cathodic species to steel surface, hence corrosion rate increasing. He also stated that flow may stimulate the removal of Fe<sup>2+</sup> ions from the steel surface yielding lower surface supersaturation and slower precipitation rates. As a result, less protective film and higher corrosion rate will be occurring.

## Effect of Temperature

Figure 9 – 13 in the Appendix show that the corrosion rates increase linearly when the temperature increase. This phenomenon is occurring for all conditions in the test. George [6] explained that this is due to acceleration of anodic and cathodic reaction rates when temperature increases. As a result, higher corrosion rate is obtained and the corrosion potential is shifted to more negative values. Furthermore, an increasing of corrosion rate at higher temperature below scaling temperature (80°C) is also due to availability of HAC species. At higher temperature, the diffusion coefficient of HAC is higher which result in more species availability, approximately a twofold increase of corrosion rate with 60 ppm HAC at 25°C than at 60°C. At room temperature, the value of diffusion coefficient of HAC is  $1.24 \times 10^{-9}$  m<sup>2</sup>/s whereas at 60°C the value is  $2.3 \times 10^{-9}$  m<sup>2</sup>/s, which is 85 % higher.

## CONCLUSION

LPR tests showed that corrosion rates increase with increasing HAC concentrations in turbulent conditions. The effect of small HAC concentrations from 10 – 60 ppm at pH 6, are more pronounced at lower speed. However, as reported by Crolet [14] HAC increases corrosion rate by extra cathodic reaction which is generated from dissociation of acetic acid and direct reduction of undissociated HAC molecules. LPR tests indirectly illustrated that there are flow dependent and flow independent that contribute to corrosion rate. At lower speed, it seems to be flow dependent, while at higher speed (4000 – 6000 rpm) the reaction is activation control. Furthermore, It is seen an increasing of corrosion rate when temperature increases. This trend occurs below scaling temperature (80°C) only. This is due to acceleration of anodic and cathodic reaction when temperature increases, also this is related with availability of HAC species which is much more at higher temperature.

## ACKNOWLEDGEMENTS

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## Appendix

### A. Effect of HAC concentrations

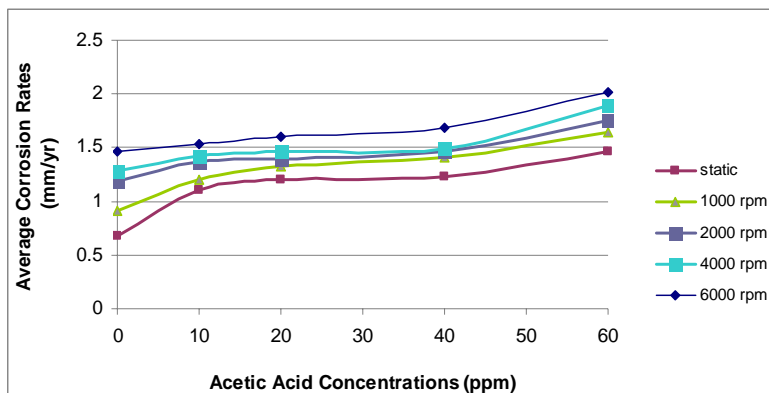


Figure 3: Corrosion trend with various HAC concentrations at pH 6, 25°C.

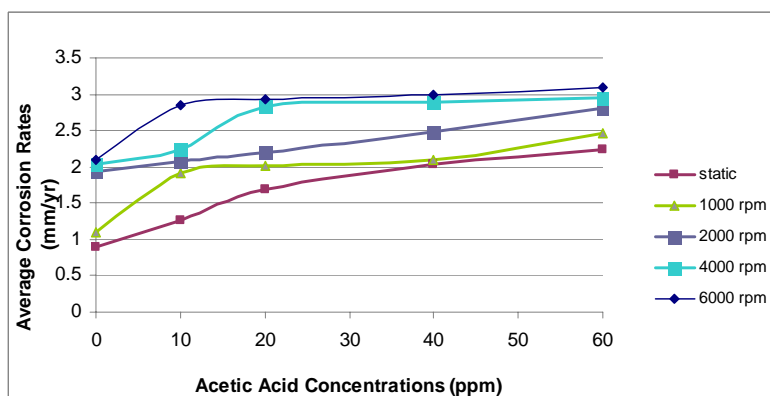


Figure 4: Corrosion trend with various HAC concentrations at pH 6, 40°C.

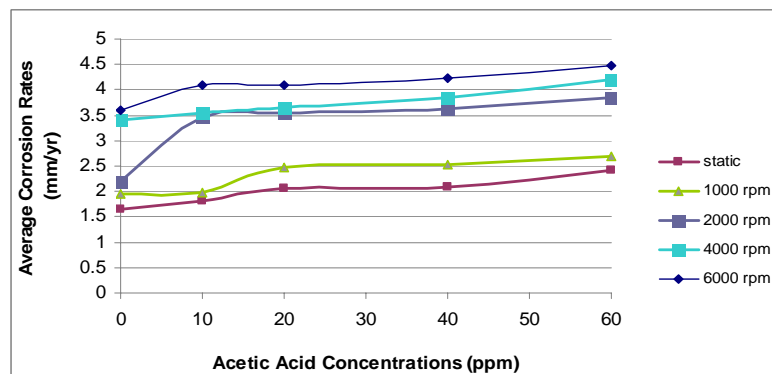


Figure 5: Corrosion trend with various HAC concentrations at pH 6, 60°C.

## B. Effect of Rotational Rates (rpm)

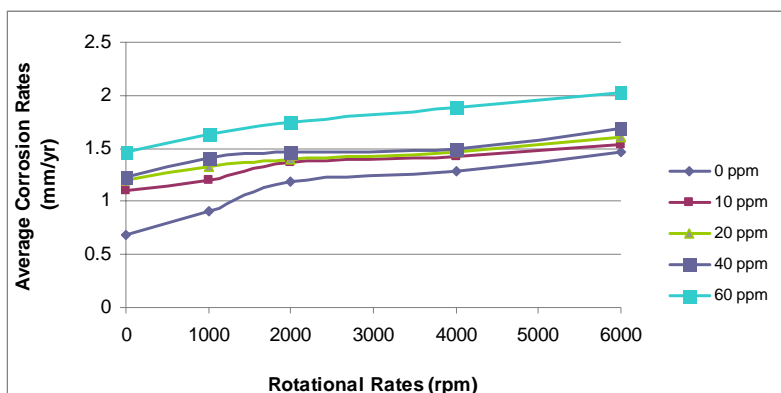


Figure 6: Corrosion trend with the increase of rotational rates (rpm) at pH 6, 25°C.

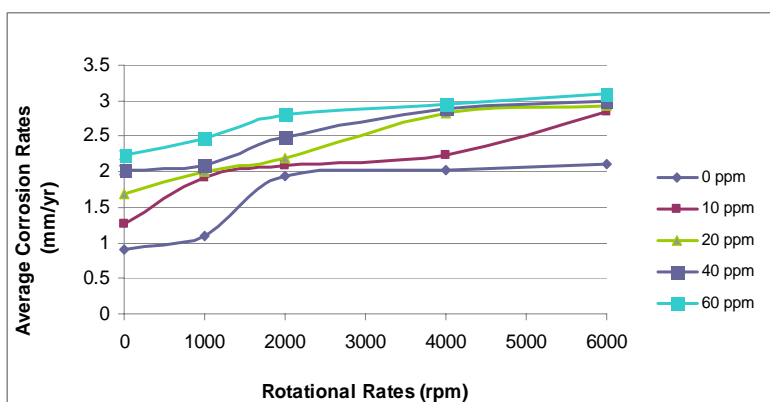


Figure 7: Corrosion trend with the increase of rotational rates (rpm) at pH 6, 40°C.

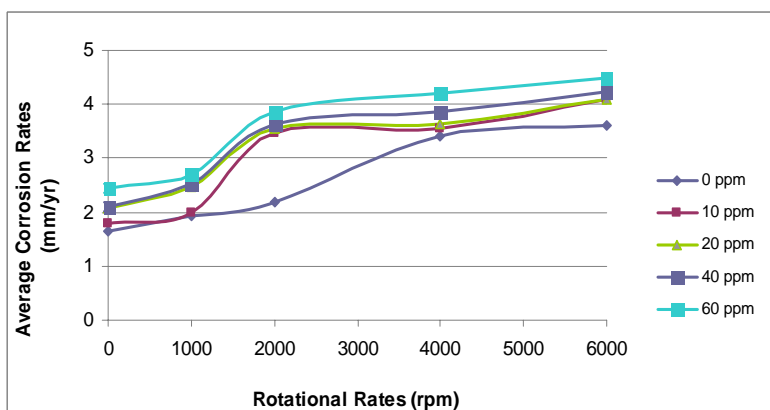


Figure 8: Corrosion trend with the increase of rotational rates (rpm) at pH 6, 60°C.



### C. Effect of Temperature

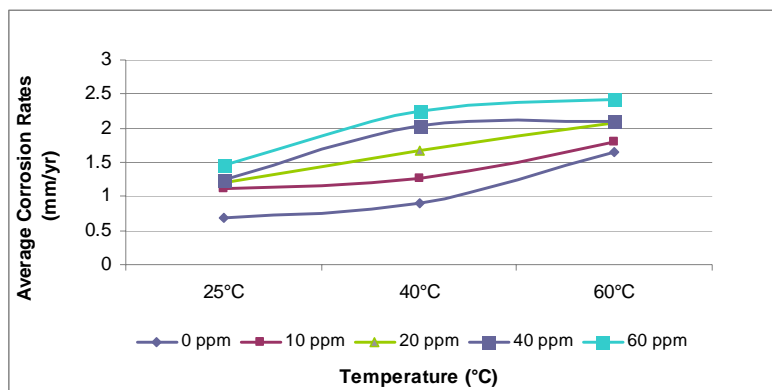


Figure 9: Average corrosion rates at static conditions with various HAC concentrations in different temperature.

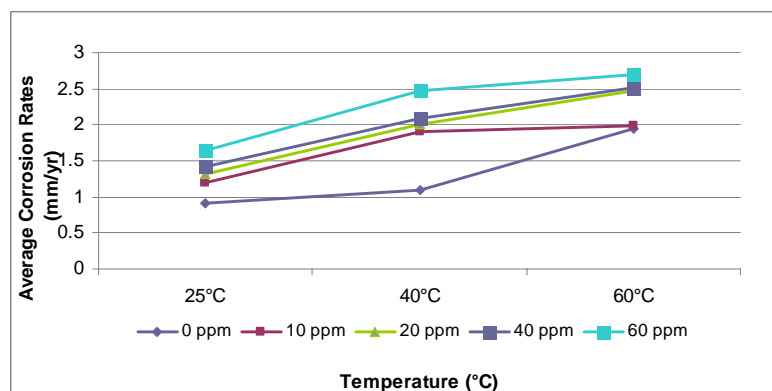


Figure 10: Average corrosion rates at 1000 rpm with various HAC concentrations in different temperature.

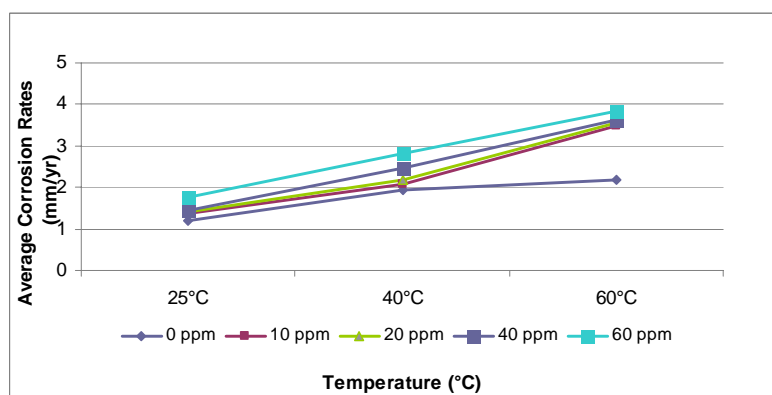


Figure 11: Average corrosion rates at 2000 rpm with various HAC concentrations in different temperature.

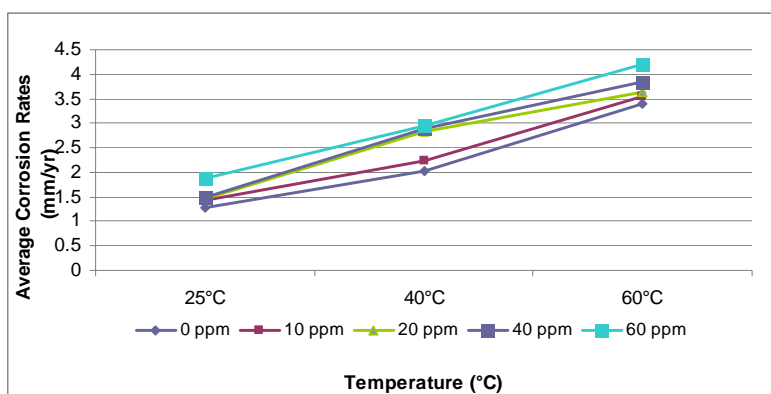


Figure 12: Average corrosion rates at 4000 rpm with various HAc concentrations in different temperature.

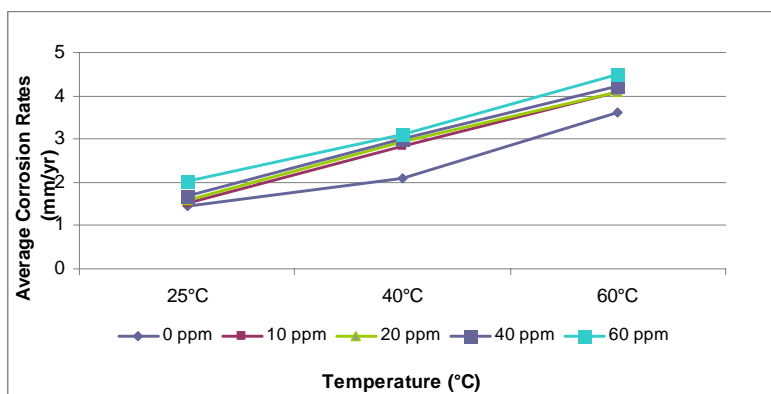


Figure 13: Average corrosion rates at 6000 rpm with various HAc concentrations in different temperature.