

CHAPTER 1

INTRODUCTION

1.1 Background Study

Corrosion cost the oil & gas industry millions of dollars every year worldwide. Corrosion is an enormous cost to these industries as measured in equipment maintenance and replacement, leaks, and system failures. These material degradations could result in the loss of mechanical properties like strength, ductility and impact strength. These could lead to loss of materials, reduction in thickness and at times ultimate failure.

Carbon dioxide systems are one of the most common environments in the oil field industry where corrosion occurs. Areas where CO₂ corrosion is most common include flowing wells, gas condensate wells, areas where water condenses, tanks filled with CO₂, saturated produced water and flowlines, which are generally corroded at a slower rate because of lower temperatures and pressures. The material of construction for pipelines in the oil and gas industry is carbon steel for majority of facilities in production installations, because of its economical price, strength, and availability. However, carbon steel has a tendency to corrode in the presence of CO₂ and HAc.

Organic acid though weak, are known to affect the rate of CO₂ corrosion to a very large amount. The quantity of organic acids in produced water in the oil and gas system is in the range of 500 to 3000 ppm of which acetic acid contributes 50 percent to 90 percent of the organic acid. Classifications of organic acid can be done on the basis of molecular weight, and it was found that the lower molecular weight organic acids such as acetic acid were primarily soluble in water and can lead to corrosion of mild steel pipelines.

1.2 Problem Statement

CO₂ corrosion in oil and gas industries is often influenced by acetic acid or HAc. Weak organic acids such as acetic acid can commonly be found in oilfield brine. The presence of organic acid such as acetic acid or HAc has been considered as the main cause of mild steel pipeline failures. In oilfield pipelines, such as in CO₂ plant the corrosion issues are usually under control and manageable. However, when small amount of organic acid that usually dominated by acetic acid, the corrosivity of the pipeline can change dramatically. Therefore it is imperative to understand the role of acetic acid in CO₂ corrosion to apply appropriate and suitable corrosion prevention in order to preserve the equipments and pipelines.

1.3 Objective and Scope of Study

The objective of this study is to understand the role and effect of different level of concentrations of acetic acid, HAc on CO₂ corrosion.

In order to achieve the objective, study of the mechanism of CO₂ corrosion in presence of acetic acid need to be done. Rate of corrosions will also be analyzed to compare the results from the experiment.

1.4 Relevance of Project

From general perspective, this topic is fully related to the engineering student which covers one small critical area in the oil and gas industries. This project could help the industry to discover the mitigation method towards corrosion to be used in order to reduce the costs and also to improve the performance of equipments in the oil and gas industry. In addition the current studies could enhance the author's knowledge and prepare for the real working culture.

CHAPTER 2

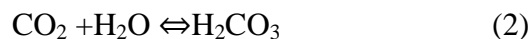
LITERATURE REVIEW

2.1 CO₂ Corrosion

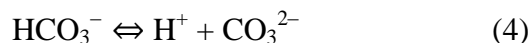
The corrosion mechanisms of CO₂ and its effects on mild steel under varying conditions of pressure, temperature, pH, and oil-water fractioning has been a widely researched topic.[1] CO₂ corrosion is a complex process as it is not only affected by the presence of multi corrosive species but also by other operational parameters such as flow, pH and material characteristic. The combined effect of these environmental and operational factors produce more aggressive environment which could result in increasing corrosion rate.[2]

Omkar (2004)[3] stated that one of the earliest efforts to explain the mechanism of CO₂ corrosion was explained by de Waard and Milliams (1975). More recent studies (1995, 2001,2003) have proposed models to predict CO₂ corrosion of mild steels based on their independent body of work. The key process of CO₂ corrosion will be shown below.

Carbon dioxide gas dissolves in water and forms a “weak” carbonic acid through hydration by water:



The carbonic acid (H₂CO₃) then partially dissociates to form the bicarbonate ion, which can further dissociate to yield the carbonate ion:



De Waard and Milliams explained that the rate determining step for carbonic acid dissociation is the direct reduction of carbonic acid (H₂CO₃) and the corrosion rate is governed

by the amount of undissociated acid in solution.[1,3] However, there are two possible cathodic reactions that can occur in the process of mild steel CO₂ corrosion: the above-mentioned direct reduction of H₂CO₃ but also reduction of hydrogen ions:[1]



The corresponding iron dissolution reaction is



The insoluble corrosion product of reactions 3, 4, and 7 is iron carbonate which forms by the reaction



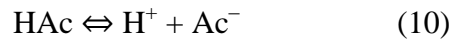
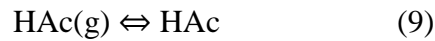
When steel corrodes in CO₂-saturated water, the solubility of iron carbonate salt (FeCO₃) may be exceeded and precipitation sets in, which increases rapidly with the degree of supersaturation and an increase in temperature. The iron carbonate precipitate may form a protective film depending on the solution composition, pressure, and temperature of the system. Other solid corrosion products may form in the presence of chlorides, sulfides, oxygen, etc. [1]

2.2 Acetic Acid Corrosion

Increasing attention has been paid to the effect of HAc on the corrosion of carbon steel over the last years. On the basis of results issued from field observations and laboratory investigations, HAc is recognized to contribute considerably to the overall corrosion rate.[3] Okafor [5] said that In 1944, the effects of organic acids and CO₂ on the corrosivity of produce water were shown by Menaul. In 1973, Obukhova reported that organic acids and CO₂ in gas condensate wells are contributing factors to high corrosion rates.

Okafor also stated that in the case of carbon steel in brine, the dominating factor influencing the corrosion rate is the presence of acetate (Ac) and dissolved CO₂ gas resulting in the formation of acetic acid. In this situation genuine acetic acid corrosion occurs, controlled by the solubility equilibrium with a gas phase containing HAc vapor, as in the case of CO₂ corrosion.[3]

When HAc is present in the system it partitions between the aqueous and the gas phases. The aqueous HAc then partly dissociates into hydrogen and acetate ions:



Iron acetate salt can form in aqueous solutions; however, its solubility is much higher than that of iron carbonate, and therefore precipitation and protective film formation by iron acetate does not readily occur. [1]

The equilibrium constant for HAc dissociation, K_{HAc} is:

$$K_{HAc} = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]} \quad (11)$$

K_{HAc} is dependent on temperature (Tc, Celcius) and was first expressed by Kharaka (1989)[1]

$$K_{HAc} = 10^{-(6.66104 - 0.0134916 * (273 + Tc) + 2.37856 * 10^{-5} * (273 + Tc)^2)} \quad (12)$$

The concentration of hydrogen ions, [H⁺] i.e. the pH determines the distribution of the acetic species in the solution i.e. how much is present in undissociated form and how much exists as acetate ion Ac⁻.

As it was clearly established in the past 9-11 that the main cause of mild steel corrosion is the undissociated (free) HAc and not the acetate ion (Ac), it is clear that the presence of organic acids is a major corrosion concern at lower pH. The distribution of acetic species with pH also explains while in some previous studies the CO₂ corrosion rate increased when acetic species were added as acetic acid (this reduced the pH) and why the CO₂ corrosion rate decreased when they were added as sodium acetate (this increased the pH). Therefore one is tempted to conclude

that at a high pH, such as pH 6.6, there should be no effect on CO₂ corrosion since almost 98% of the acetic species is present as acetate ion (Ac⁻). While this is generally true, there is a concern that the presence of organic acids somehow impairs the formation and protectiveness of iron carbonate (FeCO₃) scales.[8]

2.3 Iron Carbonate (FeCO₃) Film Formation

Iron carbonate (FeCO₃) film formation is the main corrosion product in the CO₂ corrosion proces. Film formation is strongly dependent on the thermodynamics and kinetics of FeCO₃ precipitation. Supersaturation plays the most important role in FeCO₃ film growth and its morphology. A high supersaturation of FeCO₃ is necessary to form a protective film, particularly at low temperatures[5]. In principle, the precipitation process comprises two steps, nucleation and particle growth. The morphology of the film therefore depends on the dominating step[5]. The reaction for formation of solid iron carbonate is given by:



FeCO₃ forms on the wall of the pipe if the product of ferrous ion concentration (Fe²⁺) and carbonate ion concentration (CO₃²⁻) exceeds the solubility product limit[1]. A measure of when the film is likely to precipitate is supersaturation value (SS) defined as

$$SS = \frac{[\text{Fe}^{2+}][\text{CO}_3^{2-}]}{[K_{sp} \text{FeCO}_3]} \quad (14)$$

The film will precipitate when the SS value exceeds unity. However, the rate of precipitation of iron carbonate can be so slow that often the precipitation kinetics becomes more important than the thermodynamics of the process. The equilibrium constant for iron carbonate film $K_{sp\text{FeCO}_3}$ is dependent on temperature (Tc, Celcius) and ionic strength (I) and expressed as

$$K_{sp\text{FeCO}_3} = 10^{(-10.13 - 0.0182 * Tc)} / (0.0115 * I^{0.6063}) \quad (15)$$

$$I = 0.5 * \sum nZ^2 \quad (16)$$

where I represents the number of ions, Z is charge of each ion and n is the molar concentration of each ion[1].

FeCO_3 reduces the corrosion rate by reducing and virtually sealing film porosity[5]. With altering neither the local phase compositions nor the concentration gradient, this restricts the diffusion fluxes of the species involved in the electrochemical reactions. Moreover, even prior to sealing cementite its precipitation can lead to coverage and, therefore, can limit its electrochemical activity. It is also believed that increasing the temperature would improve the protectiveness of the FeCO_3 scale as well as its adhesion and hardness and that the higher the temperature, the more improved the protectiveness[5]. However, there is a little agreement on a practical “threshold” temperature. Some have reported that the maximum corrosion rate observed for carbon steel in sweet environments was from 60°C to 70°C and then it started to decline due to growth of protective FeCO_3 films[5]. In another studies[5], it has been suggested that the lowest temperature necessary to obtain FeCO_3 films that would reduce the corrosion rate significantly was 50°C and the protectiveness was increased also by increasing the pH.

From a study, Omkar (2004)[1] mentioned that Johnson and Tomson (1991) used a “temperature ramped” approach to calculate the activation energy of FeCO_3 precipitation and found that precipitation was controlled by the surface reaction rate. The most important factors which affect the precipitation of iron carbonate film are supersaturation and temperature. The film is known to be protective and corrosion rate drops once the film starts growing. When FeCO_3 protective film forms, its growth is very temperature sensitive. Its composition, structure and thickness and physical properties are determined by the film precipitation mechanisms. A frequently used expression for the rate of precipitation of iron carbonate ($R_{\text{FeCO}_3(s)}$) is given by Van Hunnik et al. (1996) as stated by Omkar (2004)[1]

$$R_{\text{FeCO}_3(s)} = \frac{A}{V} \cdot f(T) \cdot K_{sp} \cdot f(SS) \quad (17)$$

where A is the surface area of the electrode and V is the solution volume.

Since CO_3^{2-} ion concentration is dependent on the pH, we can write

$$SS = f(\text{Fe}^{2+}, \text{pH}) \quad (18)$$

When iron carbonate precipitates at the steel surface, it decreases the corrosion rate by

- Presenting a diffusion barrier for the species involved in the corrosion process
- Blocking a portion of the steel and preventing electrochemical reactions from occurring.

Studies by Ikeda et al. (1984), as mentioned by Omkar (2004)[1] indicate three types of films: at low temperatures ($<60^{\circ}\text{C}$) the film is not adherent and is easily destroyed, at 60°C - 150°C a loosely adherent FeCO_3 precipitate causes deep pitting and very high corrosion rates, at temperatures $>150^{\circ}\text{C}$ an adherent scale forms limiting corrosion. Omkar (2004)[1] concluded that the film can be formed at room temperature by increasing system pH as indicated by Videm and Dugstad (1989). Dugstad (1992) showed that films were formed at 80°C after only 20-24 hours.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Project Activities

This section consists of project analysis where it involves data and information gathering, decide the best method or some modification on the existence methods, some case study analysis and last but not least experimental analysis.

Firstly research, collect and summarized data from the theoretical studies related to CO₂ corrosion in presence of acetic acid. Literature sources such as experimental studies, journals and reference books regarding concept of CO₂ corrosion, diagnosing the common practice techniques also contribute information to this project.

Next will be the discussion of method to study the corrosion rates of different concentration of acetic acid. With the aid of theories, the experiments will be undergone to obtain the result of the effects of different concentration of acetic acid on corrosion rate.

At the end of this study, the comparison of different rate of corrosion that have been tested will be presented in quantitative and qualitative analysis.

3.1.1 Flow Chart of Project Activities

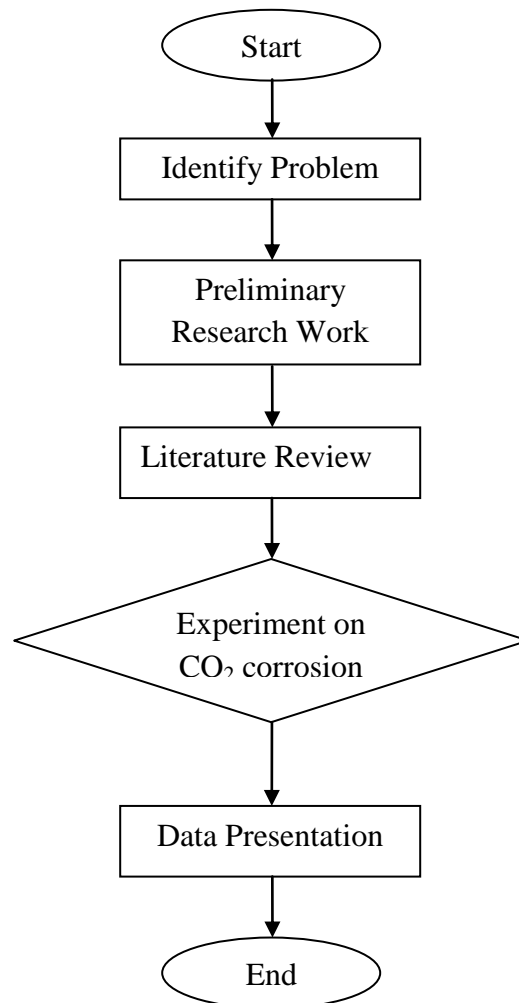


Figure 1 : Flow chart of project activities

In this project, corrosion experiments need to be done to investigate corrosion rates on different concentration of acetic acid. From the experiment, we will perform LPR and EIS test method. Further explanations on these methods will be discussed in the next section.

3.2 Test Matrix

Table 1 and Table 2 shows the test matrix of the experiment and the concentration of acetic acid at the said pH respectively :

Table 1: Test matrix for the experiment

Parameter	Value
Steel type	X-52
Solution	3% NaCl
De-oxygenation gas	CO ₂
Ph	5.5
Total HAc (ppm)	0, 1000, 2000, 4000
Temperature (°C)	60
Time (hrs)	24
Surface finish	600 grit
Measurement techniques	Linear Polarization Resistance (LPR) Electrochemical Impedance Spectroscopy (EIS)

Table 2: Acetic acid concentration at pH 5.5 and 60°C

Total Concentration (ppm)	Undissociated HAc (ppm)	Acetate concentration (ppm)
1000	154	846
2000	308	1692
4000	616	3384

Table 3: Elemental composition of X52 carbon steel based on wt %

Elements	C	Mn	P	S	Si	Nb	Cr	Ni	Al	Fe
Wt %	0.16	1.32	0.017	0.006	0.31	0.02	0.01	0.01	0.03	Balance

3.3 Experimental Setup

The schematic diagram of the setup is shown in Figure 2

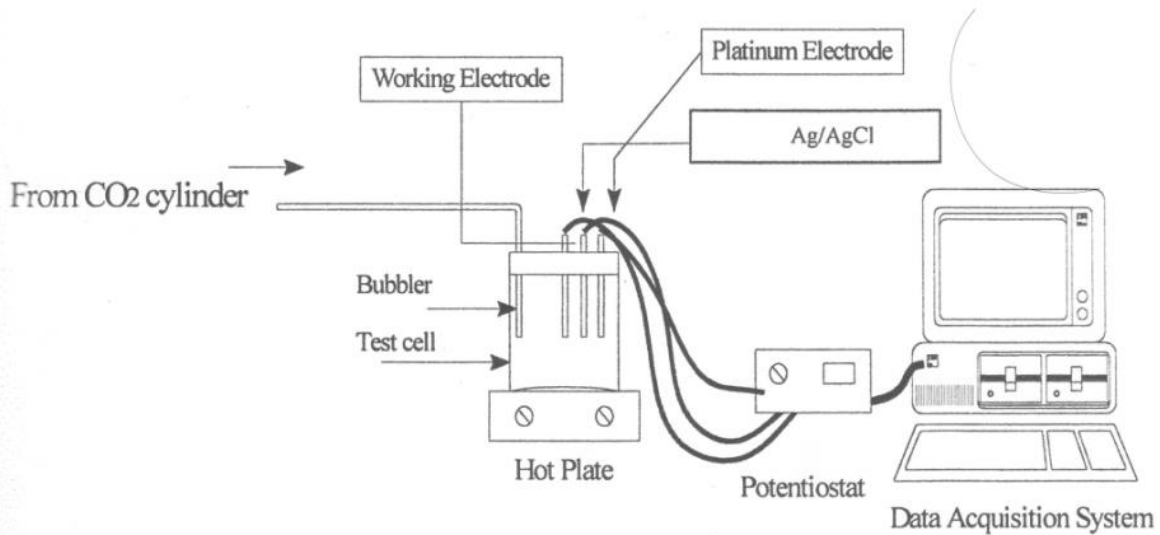


Figure 2: Schematic diagram for the set-up

3.4 Experiment Procedure

30g of NaCl was weighed and dissolved in 1000ml deionized water to produce 3 percent NaCl solution. The solution of 3% percent NaCl was poured into a glass cell where the experiment will be done.

The NaCl solution was then bubbled with CO₂ for 1 hour prior to the exposure of the electrode and maintained throughout the experiment. The purpose of the CO₂ purging is to ensure that all the oxygen is removed from the water and to maintain the saturation of CO₂. The required test temperature is also maintained throughout the experiment using a hot plate. The electrochemical measurements are based on a three-electrode system, using a commercially available potentiostat with a computer control system. The reference electrode used is an Ag/AgCl and the auxiliary electrode is a platinum electrode.

The working electrode is prepared from X52 pipeline steel (elemental composition is shown in Table 3). The sample was spot-welded with nickel-chromium wire and mounted in araldite resin with an exposed area of 0.1 cm². The sample surface is then polished to 600-grade finish using silicon carbide papers. The specimen is degreased and rinsed with ethanol and deionised water before immersion.

The sample is then immersed in the 1 liter of 3% NaCl solution which has been prepared earlier and purged with CO₂ for about 45 minutes while being heated up until the temperature reached the desired value. Then, the pH is measured and 1M of sodium bicarbonate solution is added into the solution until the pH becomes 5.5. The experiment is then ran for 0 ppm of HAc for 24 hours and the data of the LPR and EIS is collected.

The experiment is repeated for different concentrations of HAc injected as stated in the test matrix. The data collected will then be analysed.

3.4.1 Linear Polarisation Resistance (LPR)

Linear polarization resistance was used to determine the corrosion rate. Linear Polarization Resistance monitoring is an effective electrochemical method of measuring corrosion. Monitoring the relationship between electrochemical potential and current generated between electrically charged electrodes in a process stream allows the calculation of the corrosion rate. LPR is most effective in aqueous solutions, and has proven to be a rapid response technique.

Principle of Measurement

When a metal/alloy electrode is immersed in an electrolytically conducting liquid of sufficient oxidizing power, it will corrode by an electrochemical mechanism. This process involves two simultaneous complementary reactions.

At anodic sites, metal will pass from the solid surface into the adjacent solution and, in so doing, leave a surplus of electrons at the metal surface. The excess electrons will flow to nearby sites, designated cathodic sites, at which they will be consumed by oxidizing species from the corrosive liquid.

This method is based on the linear approximation of the polarization behavior at potentials near the corrosion potential. Polarisation resistance (R_p) is given by Stern-Geary equation:

$$R_p = \frac{B}{i_{corr}} = \frac{\Delta E}{\Delta I} \quad (3.1)$$

$$\text{Where, } B = \frac{b_a b_c}{2.303(b_a + b_c)} \quad (3.2)$$

The value of B used is 26 mV/decade. The corrosion current can be related directly to the corrosion rate from Faraday's law:

$$CR = \frac{315Zi_{corr}}{\rho nF} \quad (3.3)$$

where,

CR = corrosion rate, mm/year

i_{corr} = corrosion current density, $\mu\text{A}/\text{cm}^2$

ρ = density of iron, $7.8 \text{ g}/\text{cm}^3$

F = Faraday's constant, 96500 C/mole

Z = atomic weight, g/mol

n = electron number

b_a, b_c = the slopes of the logarithmic local anodic and cathodic polarization curves respectively

Rp = resistance polarization, ohm

Linear polarization resistance measurements were performed by firstly measuring the corrosion potential of the exposed sample and subsequently sweeping from -10mV to +10mV with the sweep rate of 10mV/min.

3.4.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy or EIS is a powerful technique for the characterization of electrochemical systems. The promise of EIS is that, with a single experimental procedure encompassing a sufficiently broad range of frequencies, the influence of the governing physical and chemical phenomena may be isolated and distinguished at a given applied potential.

A typical electrochemical impedance experimental set-up consists of an electrochemical cell (the system under investigation), a potentiostat/galvanostat, and a frequency response analyser (FRA). The FRA applies the sine wave and analyses the response of the system to determine the impedance of the system.

The electrochemical cell in an impedance experiment can consist of two, three, or four electrodes. Usually the electrode under investigation is called the working electrode, and the electrode necessary to close the electrical circuit is called the counter electrode. The electrodes are usually immersed in a liquid electrolyte. For solid-state systems, there may be a solid electrolyte or no electrolyte. In this experiment, three electrode systems are used which are the working electrode, the reference electrode, and the auxiliary electrode.

EIS measurements can be done in the potentiostatic or galvanostatic mode. In the potentiostatic mode, experiments are done at a fixed DC potential. A sinusoidal potential perturbation is superimposed on the DC potential and applied to the cell. The resulting current is measured to determine the impedance of the system. [12]

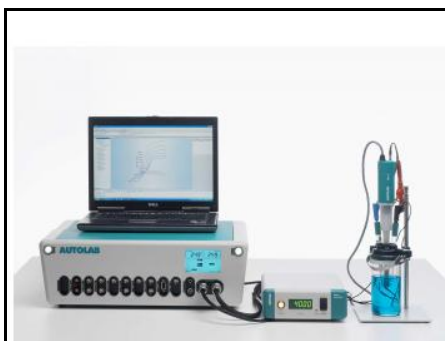


Figure 3 : Image of Test Setup

3.5 Final Year Project 2 Gantt Chart

NO	ACTIVITIES	WEEK NO/MONTH																		
		SEPTEMBER				OKTOBER				NOVEMBER				DECEMBER				JANUARY		
				1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	
1	Experimental Work Continues																			
	1.1 Sample preparation			■	■															
	1.2 Run experiment (LPR & EIS)				■	■	■	■	■	■										
	1.3 Data gathering and result analysis									■	■									
2	Progress Report																			
	2.1 Submission of progress report											Δ								
3	Experimental Work Continues																			
	3.1 Run experiment												■	■						
	3.2 FESEM analysis													■						
	3.3 XPS analysis														■					
4	Pre-EDX																			
	4.1 Submission of poster														Δ					
5	Dissertation & Oral Presentation																			
	5.1 Submission of draft report																Δ			
	5.2 Submission of dissertation (soft bound)																	Δ		
	5.3 Submission of technical paper																	Δ		
	5.4 Oral presentation																		Δ	
	5.5 Submission of project dissertation (hard bound)																			Δ

Legend: Δ key milestone

■ Progress bar

CHAPTER 4

RESULT AND DISCUSSION

4.1 Data Gathering & Analysis

The next step is obtaining the results from the experiment. The results obtained from the experiment were collected and analyze using the linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) techniques. The effects of various concentrations of acetic acid (HAc) from 0 to 4000 ppm on the corrosion behavior of X52 carbon steel in 3% NaCl solution saturated with CO₂ in this experiment are presented below.

4.1.1 Linear Polarization Resistance (LPR) Test

1. Effect of 0 ppm HAc

The effect of 0 ppm HAc, or in the absence of HAc, on the corrosion rate at pH 5.5 and temperature 60°C after 24 hours is shown in Figure 4. For concentration of 0ppm HAc the corrosion rates obtained are in a range of 0.5 mm/yr to 2.5 mm/yr.

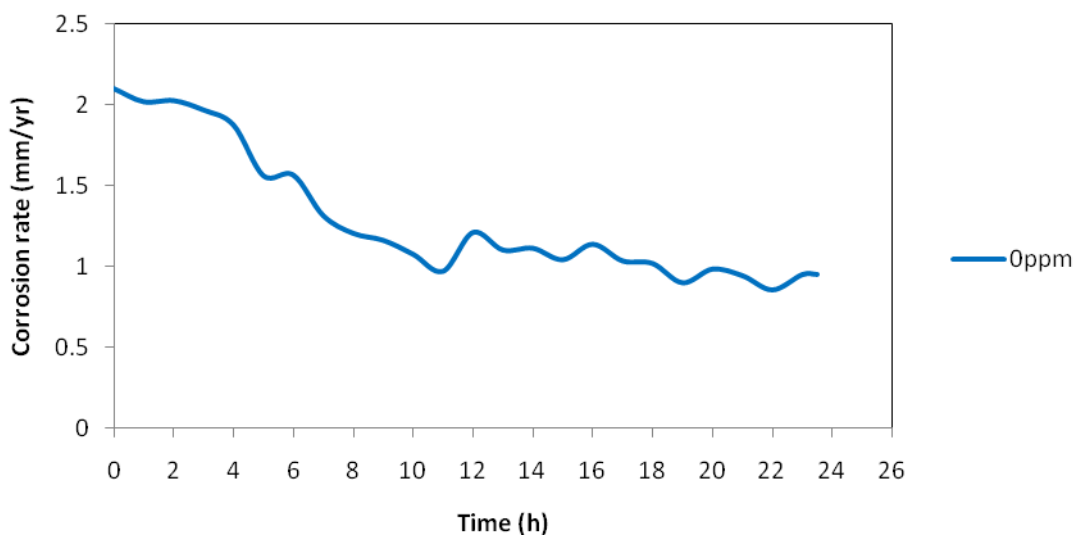


Figure 4: Corrosion rate at 0 ppm of HAc

2. Effect of 1000 ppm HAc

The effect of 1000 ppm HAc, on the corrosion rate at pH 5.5 and temperature 60°C after 24 hours as obtained by the LPR test is shown in Figure 5. For concentration of 1000 ppm of HAc, it is seen that the corrosion rates increased. Initially, the corrosion rate obtained was 6mm/yr and decreased in time to 1.5mm/yr.

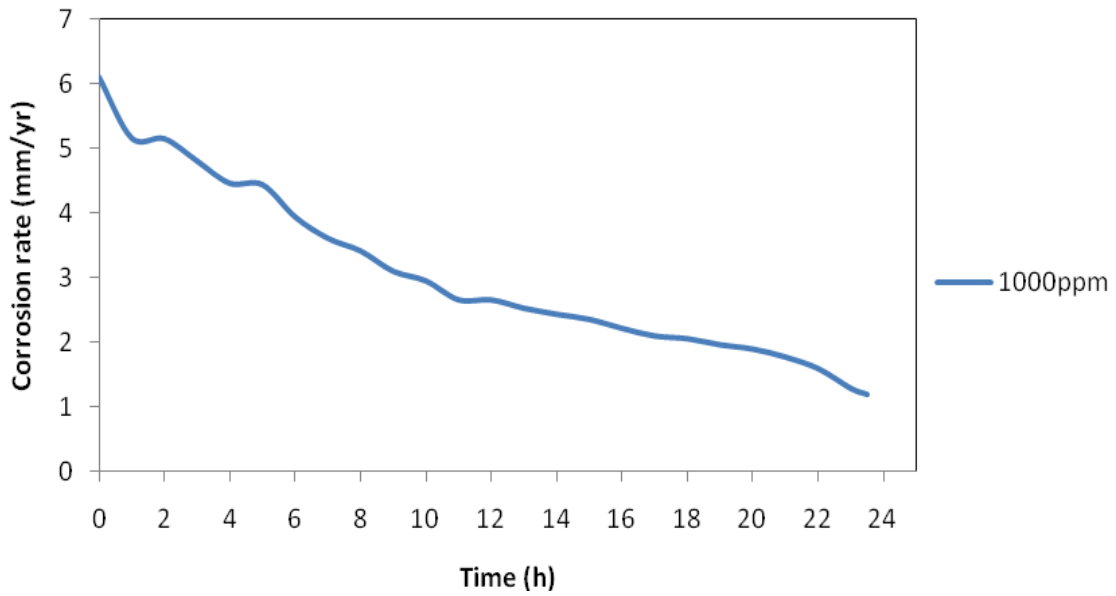


Figure 5: Corrosion rate at 1000 ppm of HAc

3. Effect of 2000 ppm HAc

The effect of 2000 ppm HAc, on the corrosion rate at pH 5.5 and temperature 60°C after 24 hours as obtained by the LPR test is shown in Figure 6. For concentration of 2000 ppm of HAc, it is seen that the corrosion rates increased. Initially, the corrosion rate obtained was around 7.5mm/yr and decreased in time to 2 mm/yr.

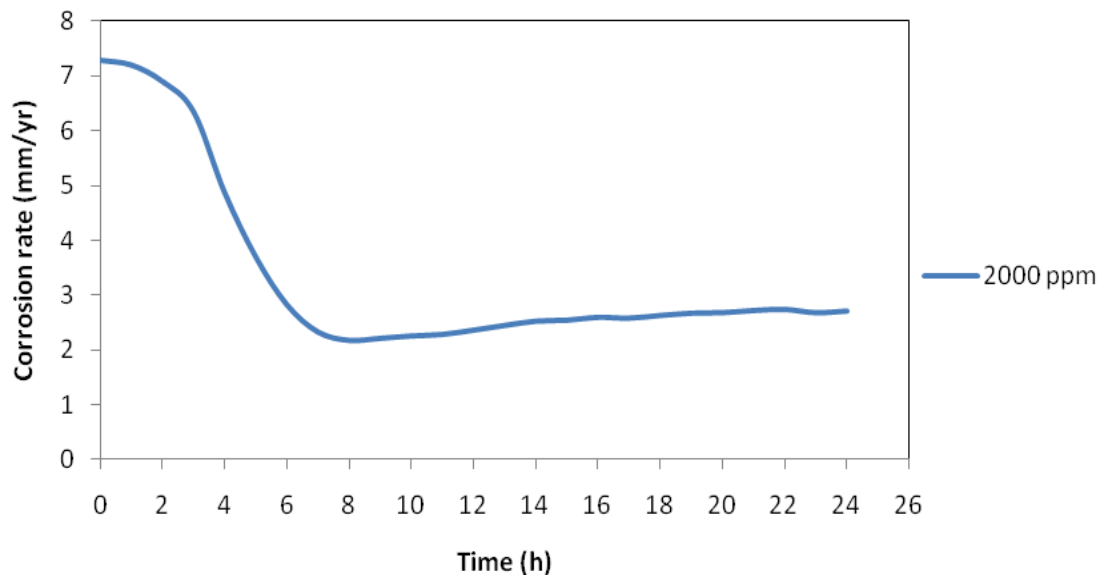


Figure 6: Corrosion rate at 2000 ppm of HAc

4. Effect of 4000 ppm HAc

The effect of 4000 ppm HAc, on the corrosion rate at pH 5.5 and temperature 60°C after 24 hours as obtained by the LPR test is shown in Figure 7. It is seen that for 4000ppm of HAc, the corrosion rates decreased as to compared with 1000 ppm and 2000 ppm. Initially, the corrosion rate obtained was around 3mm/yr and decreased in time to 1mm/yr

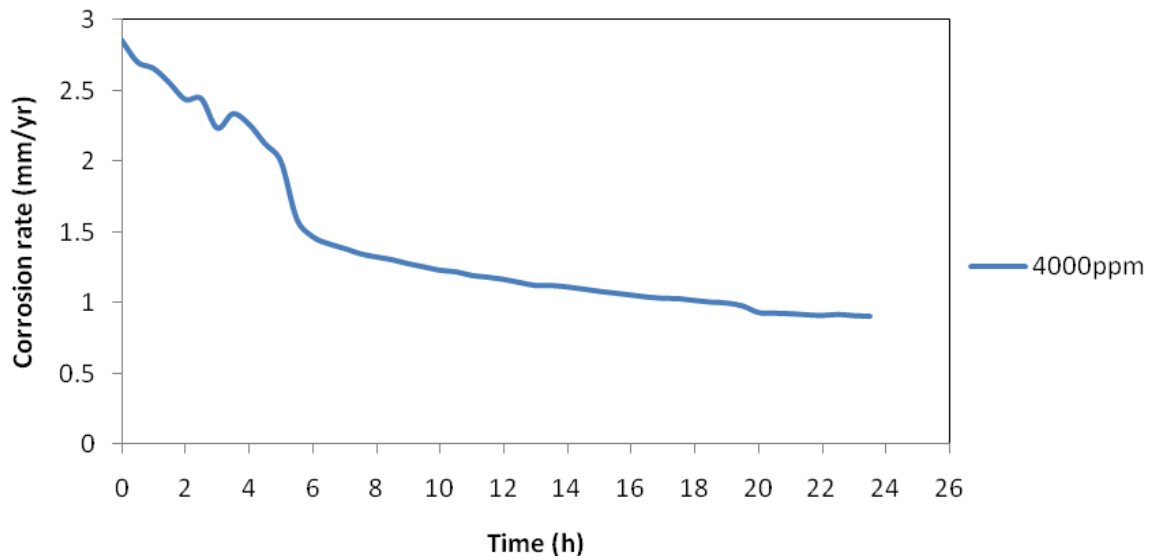


Figure 6: Corrosion rate at 4000 ppm of HAc

4.1.2 Average corrosion rate of different concentration of HAc

Figure 7 below will show the average corrosion rate for X52 steel exposed to different concentration of 0ppm to 4000ppm.

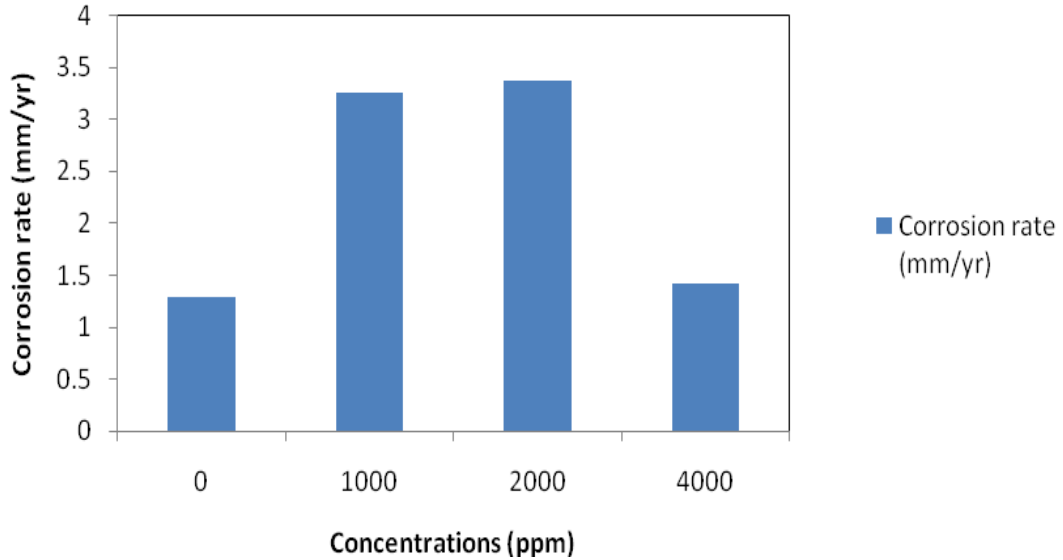


Figure 7: Average corrosion rate at different concentration of HAc

It is seen that the concentration for 1000ppm and 2000ppm caused higher corrosion rate than blank CO₂ which are around 3 and 3.5 mm/year. However, the corrosion rate decreased to less than 1.5 mm/year with the addition of 4000 ppm of acetic acid.

4.1.3 Comparison of corrosion rate with different time duration

In this section, comparison of trends obtained from graphs showing corrosion rates with function of time will be shown. In previous study a similar LPR testing have been done with different duration of time. The duration for the glass-cell experiment for the previous study was 2 hours compared to 24 hours.

The effect of different concentration of HAc, on the corrosion rate at pH 5.5 and temperature 60°C after 2 hours and 24 hours as obtained by the LPR test is shown in figure below.

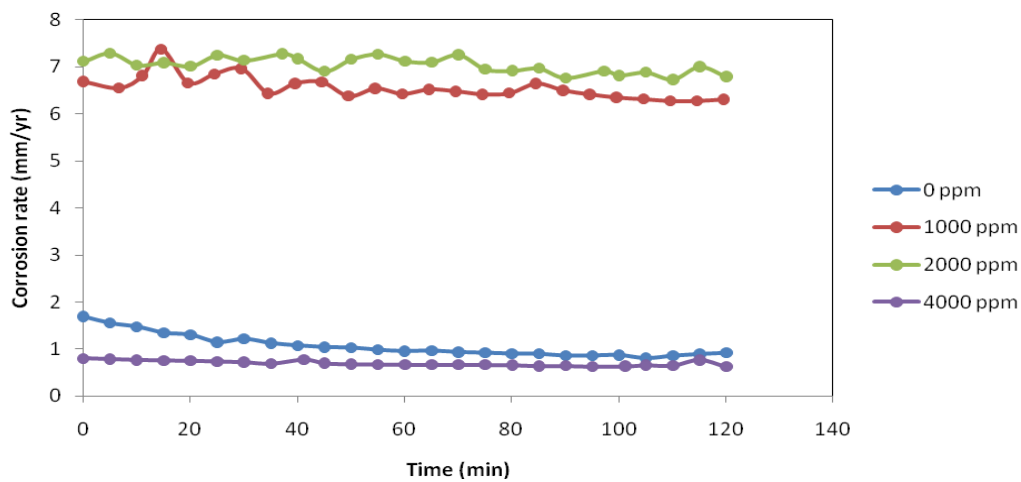


Figure 9: Corrosion rate at different concentration of HAc at 60C with pH 5.5 for 2 hours

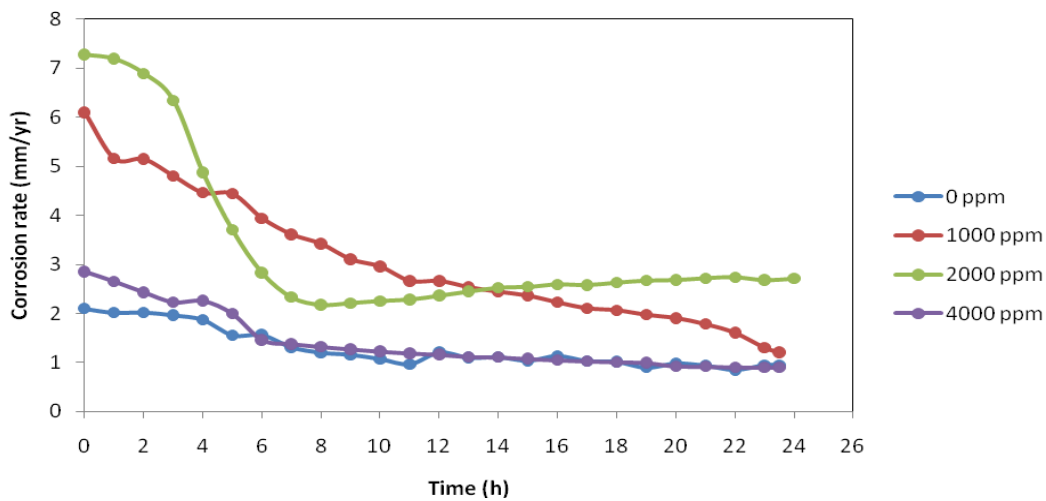


Figure 10: Corrosion rate at different concentration of HAc at 60C with pH 5.5 for 24 hours.

Comparison of average reading of corrosion rate obtained from LPR test for different concentration in 2 hours duration and 24 hours duration.

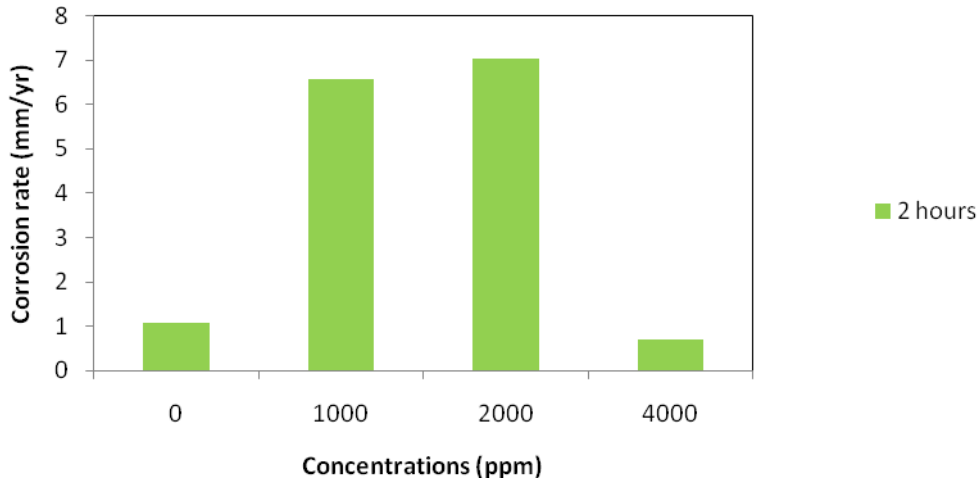


Figure 11: Average corrosion rate at different concentration of HAc for 2 hours

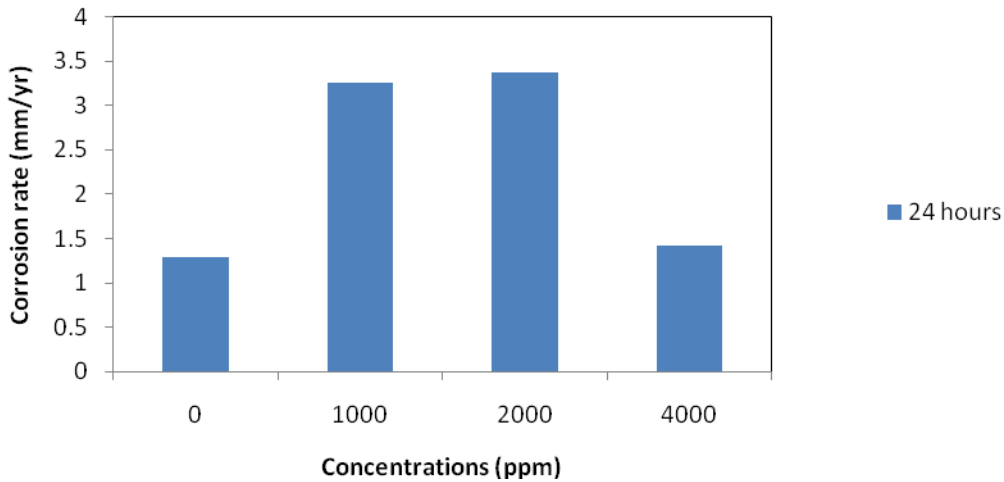


Figure 12: Average corrosion rate at different concentration of HAc for 24 hours

Based on the results that we obtain we can see that the corrosion rate increases significantly for concentration of 1000ppm and 2000ppm compare to 0ppm. This contributes to a lower Fe^{2+} supersaturation in the corrosion film and at the steel surface. The presence of acetate ions (Ac^-) in acetic acid also is prone to solubilize the dissolving iron of ions (Fe^{2+}) and suppress iron carbonate layer which can deactivate the steel surface. The reaction of Fe^{2+} and Ac^- occurs at a high rate and forms iron(II) acetate (FeAc) which is highly soluble in water.

On the other hand, the iron carbonate (FeCO_3) that was formed from Fe^{2+} and CO_3^{2-} occurs at a very slow rate as compared to that of FeAc . Therefore, more Fe^{2+} ions will react with Ac^- . As the concentration of acetic acid increase, the solubility of iron acetate is also increased even the pH is maintained.. Thus, the rate of corrosion increased as the exposed area of the carbon steel increase when the solubility of iron acetate increased.

However, all three graphs shows significant decrease within hours and then the corrosion rate was maintained back to previous rate. Since the corrosion rate only temporarily increased with addition of acetic acid and eventually returned to the low values it had before, it was assumed that the protective iron carbonate layer was not affected by the acid.

4.1.2 Electrochemical Impedance Spectroscopy (EIS)

The Nyquist plots obtained for the sample at different concentration of HAc injected at pH 5.5 and temperature 60°C after 24 hours are shown below.

4.1.2.1 Effect of 0 ppm HAc

The Nyquist plot of 0 ppm HAc, or in the absence of HAc, at pH 5.5 and temperature 60°C after 24 hours is shown in Figure 13.

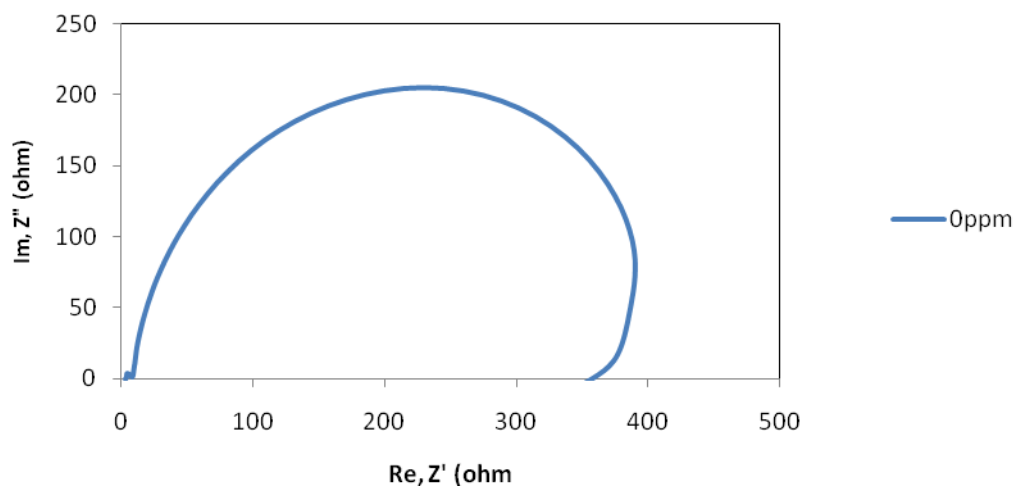


Figure 13: Nyquist plot at 0 ppm of HAc

4.1.2.2 Effect of 1000 ppm HAc

The Nyquist plot of 1000 ppm HAc at pH 5.5 and temperature 60°C after 24 hours obtained by the EIS test is shown in Figure 14.

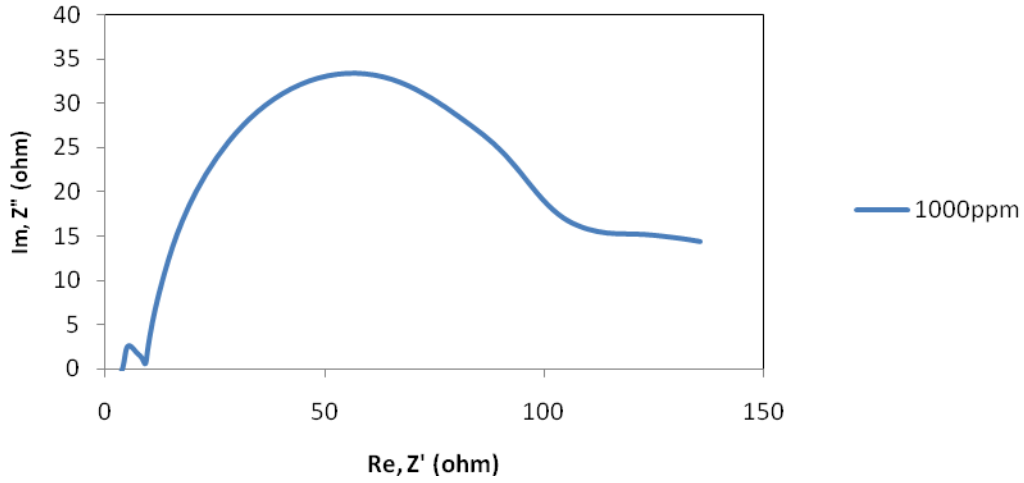


Figure 14: Nyquist plot at 1000 ppm of HAc

4.1.2.3 Effect of 2000 ppm HAc

The Nyquist plot of 2000 ppm HAc at pH 5.5 and temperature 60°C after 24 hours obtained by the EIS test is shown in Figure 15.

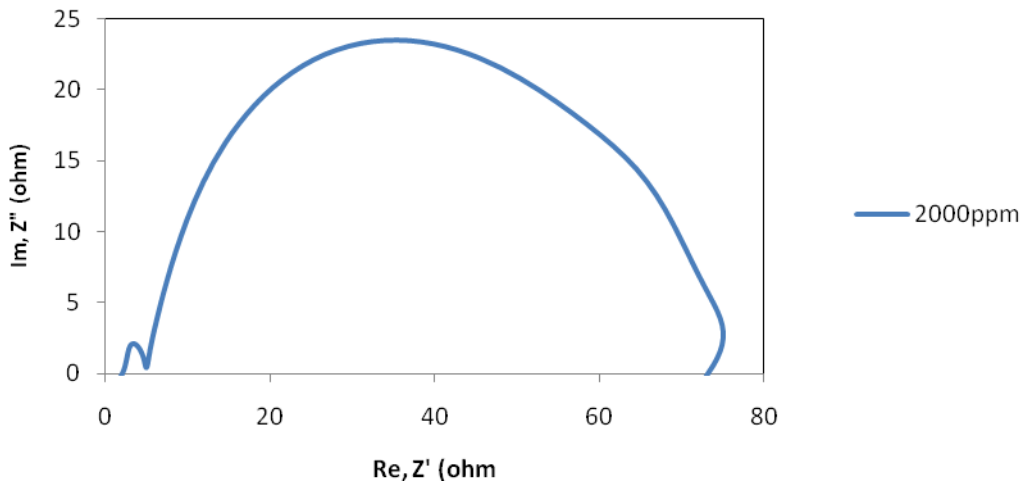


Figure 15: Nyquist plot at 2000 ppm of HAc

4.1.2.4 Effect of 4000 ppm HAc

The Nyquist plot of 4000 ppm HAc at pH 5.5 and temperature 60°C after 2 hours obtained by the EIS test is shown in Figure 16.

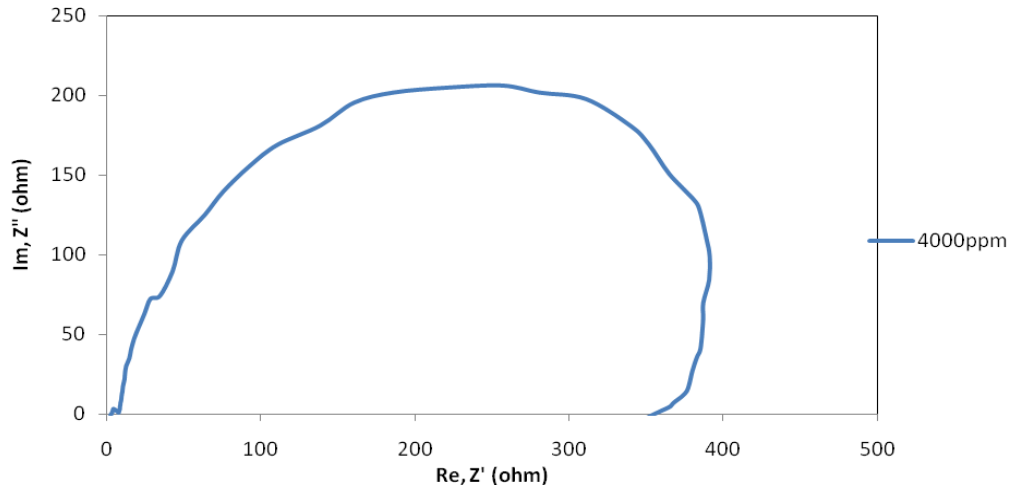


Figure 16: Nyquist plot at 4000 ppm of HAc

4.1.2.5 Comparison of the effect of HAc concentrations

The comparison of the Nyquist plot of 4 different concentrations of HAc at pH 5.5 and temperature 60°C after 24 hours obtained by the EIS test is shown in Figure 17.

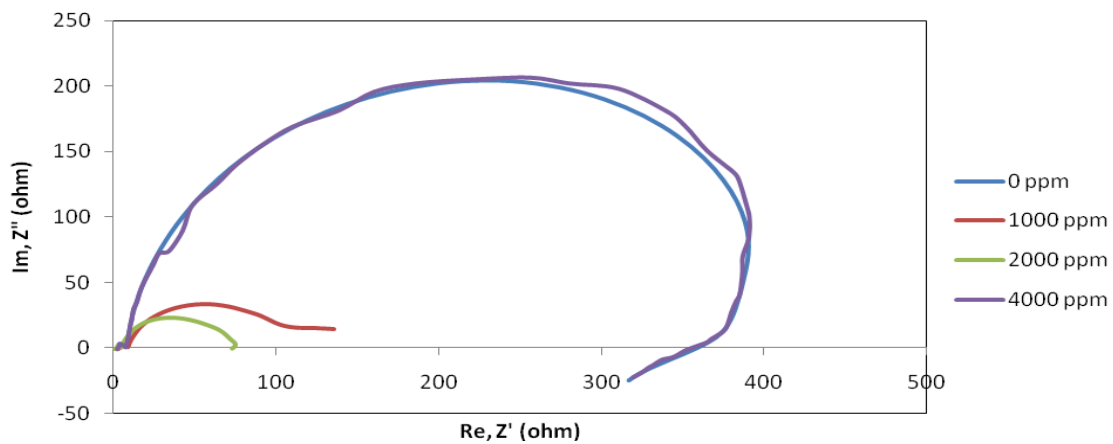


Figure 17: Nyquist plot of the effect of HAc at four different concentrations

Figure 17 shows a very large capacitive loop in the blank solution (0 ppm) and could be considered as the capacitance of double electrode layer between the corrosion scale and solution. This is followed by another capacitive loop for other concentrations of acetic acid.

It is known that iron carbonate film or layer will form and act as a protective scale on the surface of the steel surface if the reaction is given long and enough time to react, preventing the corrosion from happening. When the layer is completely compact, the corrosion is controlled by a diffusion process. However, if there are some pores in the layer, a charge transfer process at the layer/steel interface occurs. This will change the corrosion mechanism to the charge transfer and the shape of impedance plot at low frequencies to a capacitive loop.

At 1000 ppm of acetic acid, the capacitive loop at diminished significantly and the loop became smaller. It could be seen from the plots that there was a drastic decrease of the impedance values in the presence of 1000 ppm of acetic acid. The shrinkage of the loops shows an increase in corrosion rate and therefore a decrease in the protectiveness of iron carbonate layer. Therefore, active species, such as FeAc, could get to the steel surface easier resulting in an increase of the corrosion rate.

When the concentration of acetic acid is increased to 2000 ppm, the capacitive loop became much smaller than the previous condition as the impedance is diminished. As stated earlier, the shrinkage of the loop means even much less protective iron carbonate layer and an increase in the corrosion rate.

On the other hand, in the presence of 4000 ppm of acetic acid, the capacitive loop expanded and the values of the impedance became bigger. This results from an excessive amount of concentration of undissociated acetic acid injected into the solution. The excessive Ac^- ions from the acid reacts with the Fe^{2+} ions from the steel as the rate of reaction of these ions are much higher than that of FeCO_3 . This reaction, which forms in a much higher rate than its solubility, will form iron acetate (FeAc) which will act as another protective layer on the steel surface, thus, reducing the corrosion rate.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

Based on the results obtained, the corrosion rate increased with the addition of 1000 ppm and 2000 ppm of acetic acid. However, with the addition of 4000 ppm of acetic acid, the corrosion rate decreased.

In the presence of 1000 ppm of acetic acid, the corrosion rate started to increase as the acetate ions from the acid tends to solubilize the dissolving iron ions and suppress iron carbonate layer which can passivate the steel surface. The solubility of iron acetate increases as the concentration of acetic acid increases. Thus, the presence of 2000 ppm of acetic acid will expose the surface of the steel even more and increase the corrosion rate.

On the other hand, in the presence of 4000 ppm of acetic acid, the corrosion rate decreased significantly and is believed due to the excessive amount of concentration of acetate ions in the solution. The carbonate ions from the iron carbonate could not dissolve the excessive amount of acetate leaving the iron ions to reacts with it and form iron acetate. However, it is still not clear how the iron acetate compound will affect the steel surface.

It is recommended that the energy dispersive x-ray (EDX) analysis also should be done in order to confirm the presence of any compound on the steel surface.

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